

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

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INTERNATIONAL APPLICATION NO.
PCT/JP99/07344INTERNATIONAL FILING DATE
27 December 1999PRIORITY DATE CLAIMED
28 December 1998

TITLE OF INVENTION

LAMINATE AND ITS PRODUCTION METHOD

APPLICANT(S) FOR DO/EO/US

TACHIBANA Yuko et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice for Consideration of Documents Cited in International Search Report/Notice of Priority/PCT/IB/304
Drawings (21 Sheets)/PCT/IB/308

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.492(a)(1)-(5)) :- 09/857209	INTERNATIONAL APPLICATION NO. PCT/JP99/07344	ATTORNEY'S DOCKET NUMBER 209663US0PCT
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24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :-

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **\$1000.00**
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **\$860.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$710.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$690.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =**\$860.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	10 - 20 =	0	x \$18.00	\$0.00
Independent claims	2 - 3 =	0	x \$80.00	\$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00

TOTAL OF ABOVE CALCULATIONS =**\$860.00**

☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

\$0.00**SUBTOTAL =****\$860.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

\$0.00**TOTAL NATIONAL FEE =****\$860.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

\$0.00**TOTAL FEES ENCLOSED =****\$860.00**

Amount to be refunded	\$
charged	\$

- a. ☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030**. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**22850**

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SIGNATURE

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NAME

24,618

REGISTRATION NUMBER

6-22-01

DATE

09/857259

531 Rec'd PCT 22 JUN 2001

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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
YUKO TACHIBANA : ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN. :
(Based on PCT/JP99/07344)
FILED: HEREWITH :
FOR: LAMINATE AND ITS :
PRODUCTION METHOD

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

3. (Amended) The laminate according to Claim 1, wherein the interlayer is a layer consisting of at least one member selected from the group consisting of an oxide, a nitride, an oxynitride, a carbide and a boride.

4. (Amended) The laminate according to Claim 1, wherein the thickness of the interlayer is from 0.1 to 30 nm.

5. (Amended) The laminate according to Claim 1, wherein the metal layer is a layer containing at least one metal selected from the group consisting of silver, copper and gold.

6. (Amended) The laminate according to Claim 1, wherein the sheet resistance value is from 0.5 to 3.5 Ω/\square , the visible light transmittance is at least 40%, and the visible light reflectance is at most 10%.

7. (Amended) The laminate according to Claim 1, wherein a resin film having a low-reflecting property is further laminated thereon.

8. (Amended) The laminate according to Claim 1, wherein a resin film having an near-infrared shielding property is further laminated thereon.

9. (Amended) The laminate according to Claim 1, wherein the visible light reflectance is at most 3%.

REMARKS

Claims 1-10 are active in the present application. Claims 3-9 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

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Marked-Up Copy

Serial No:

Amendment Filed on:

6-22-01

IN THE CLAIMS

--3. (Amended) The laminate according to Claim 1[or 2], wherein the interlayer is a layer consisting of at least one member selected from the group consisting of an oxide, a nitride, an oxynitride, a carbide and a boride.

4. (Amended) The laminate according to [any one of Claims 1 to 3] Claim 1, wherein the thickness of the interlayer is from 0.1 to 30 nm.

5. (Amended) The laminate according to [any one of Claims 1 to 4] Claim 1, wherein the metal layer is a layer containing at least one metal selected from the group consisting of silver, copper and gold.

6. (Amended) The laminate according to [any one of Claims 1 to 5] Claim 1, wherein the sheet resistance value is from 0.5 to 3.5 Ω/\square , the visible light transmittance is at least 40%, and the visible light reflectance is at most 10%.

7. (Amended) The laminate according to [any one of Claims 1 to 6] Claim 1, wherein a resin film having a low-reflecting property is further laminated thereon.

8. (Amended) The laminate according to [any one of Claims 1 to 7] Claim 1, wherein a resin film having an near-infrared shielding property is further laminated thereon.

9. (Amended) The laminate according to [any one of Claims 5 to 8] Claim 1, wherein the visible light reflectance is at most 3%.--

DESCRIPTION

LAMINATE AND ITS PRODUCTION METHOD

TECHNICAL FIELD

The present invention relates to a laminate having
5 titanium oxide layers and its production method.

BACKGROUND ART

A laminate having metal layers laminated on a
transparent substrate such as glass (hereinafter referred
to as "metal-containing laminate") is widely used for
10 e.g. window glass of buildings and automobiles with a
purpose of e.g. suppressing emission of heat ray to
decrease a load on air conditioning. Further, the metal-
containing laminate is used also as a shielding material
to suppress leakage of electromagnetic wave radiating
15 from an apparatus such as a plasma display.

In a case where the metal-containing laminate is
applied to e.g. window glass, a high visible light
transmittance is required together with a small emission
of heat ray, and at the same time, a low visible light
20 reflectance and a preferred reflection color tone are
required.

Further, in a case where the metal-containing
laminate is used as an electromagnetic wave shielding
material, together with a high electrical conductivity, a
25 visible light transmittance as high as possible and a
visible light reflectance as low as possible, and
further, a preferred reflection color tone are required.

With respect to the metal-containing laminate, it is required that the wavelength range showing a low reflectance is broad in the visible light region in order to obtain a low visible light reflectance and a preferred reflection color tone.

Further, it is well known that a laminate having a layer constitution wherein dielectric material layers and metal layers are alternately laminated one on another is suitable to obtain a high visible light transmittance together with a low emissivity and an electrical conductivity.

A low heat ray emissivity (i.e. a high electrical conductivity) alone can be obtained by making the metal layer thick. However, it may cause decrease in the visible light transmittance and increase in the visible light reflectance. Further, the wavelength range in which a low reflectance can be obtained in the visible light region tends to be narrow, whereby a preferred reflection color tone may be impaired.

It is generally known that a phenomenon caused by making the metal layer thick (the above unfavorable phenomenon that the reflection color tone is impaired) can be diminished in a case where a material having a high refractive index such as titanium oxide is used as the dielectric material layer, as compared with a case where a material having a refractive index lower than that of titanium oxide is used.

Further, it is generally known that the phenomenon caused by making the metal layer thick can be diminished also in a case where the number of lamination is increased.

5 Actually, when a laminate is constituted by using titanium oxide layers as the dielectric material layers, the wavelength width in which a low reflectance can be obtained in the visible light region can be broadened as compared with a case of using a material having a
10 refractive index lower than that of titanium oxide, whereby a more preferred reflection color tone can be obtained. However, there is such a problem that the visible light transmittance tends to decrease, and further, the rate of decrease in the visible light
15 transmittance tends to increase together with the increase in the number of lamination.

Further, there is such a problem that a laminate constituted by using titanium oxide layers as the dielectric material layers has a low abrasion resistance.

20 It is an object of the present invention to improve the transmittance in the visible light region with respect to a laminate employing a titanium oxide.

Further, it is an object of the present invention to improve abrasion resistance with respect to a laminate
25 employing a titanium oxide.

DISCLOSURE OF THE INVENTION

The present invention provides a laminate which

comprises a substrate, and a titanium oxide layer, a metal layer and a titanium oxide layer laminated alternately in this order on the substrate in $(2n + 1)$ layers (wherein n is a positive integer), wherein an interlayer having a refractive index of less than 2.4 at a wavelength of 550 nm is interposed at at least one interlaminar boundary between the titanium oxide layer and the metal layer.

The present invention further provides a method for producing a laminate comprising a substrate, and a titanium oxide layer, a metal layer and a titanium oxide layer laminated alternately in this order on the substrate in $(2n + 1)$ layers (wherein n is a positive integer), which comprises a step of interposing an interlayer having a refractive index of less than 2.4 at a wavelength of 550 nm at at least one interlaminar boundary between the titanium oxide layer and the metal layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 1 to 5, 18 to 19, 63 to 68 and 81 to 89.

Fig. 2 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Comparative Example 1.

Fig. 3 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced

in Examples 6 to 12, 20 to 21, 69 to 72, 90 to 100, 122 to 126 and 127 to 131.

Fig. 4 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 13 to 17 and 73 to 80.

Fig. 5 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Comparative Examples 2 to 3.

Fig. 6 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Comparative Examples 4 to 5.

Fig. 7 is a diagram illustrating the relation between thicknesses of interlayers and visible light transmittances of laminates produced in Examples 1 to 17.

Fig. 8 is a diagram illustrating visible spectral characteristics of laminates produced in Examples 1 to 2 and Comparative Example 1.

Fig. 9 is a diagram illustrating visible spectral characteristics of laminates produced in Examples 6 and 8 and Comparative Example 1.

Fig. 10 is a diagram illustrating visible spectral characteristics of laminates produced in Examples 13 to 15 and Comparative Example 1.

Fig. 11 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 22 to 23 and 101 to 102.

Fig. 12 is a diagrammatical cross-sectional view

illustrating a layer constitution of laminate produced in Comparative Example 6.

Fig. 13 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 24 to 25 and 103 to 104.

Fig. 14 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 26 to 27 and 105 to 106.

Fig. 15 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 28 to 29 and 107 to 108.

Fig. 16 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 30 to 31 and 109 to 110.

Fig. 17 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 32 to 33 and 111 to 112.

Fig. 18 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 34 to 35 and 113 to 114.

Fig. 19 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 36 to 37 and 115 to 116.

Fig. 20 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 38 to 40 and 117 to 121.

Fig. 21 is a diagram illustrating visible spectral

characteristics of laminates produced in Examples 38 to 40 and Comparative Example 6.

Fig. 22 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 41 to 42.

Fig. 23 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Example 43.

Fig. 24 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Comparative Example 7.

Fig. 25 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Example 44.

Fig. 26 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Example 45.

Fig. 27 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 46 to 47.

Fig. 28 is a diagrammatical cross-sectional view illustrating a layer constitution of laminates produced in Examples 48 to 54.

Fig. 29 is a diagrammatical cross-sectional view illustrating a layer constitution of a laminate produced in Comparative Example 9.

Fig. 30 is a diagram illustrating the relation

between sheet resistance values and visible light transmittances of laminates produced in Examples 48 to 50 and Comparative Examples 9 to 11.

Fig. 31 is a diagram illustrating the relation
5 between sheet resistance values and visible light reflectances of laminates produced in Examples 48 to 50 and Comparative Examples 9 to 11.

Fig. 32 is a diagrammatical cross-sectional view
10 illustrating a layer constitution of laminates produced in Examples 55 to 57.

Fig. 33 is a diagram illustrating the relation
between sheet resistance values and visible light transmittances of laminates produced in Examples 55 to 57 and Comparative Examples 12 to 14.

15 Fig. 34 is a diagram illustrating the relation between sheet resistance values and visible light reflectances of laminates produced in Examples 55 to 57 and Comparative Examples 12 to 14.

BEST MODE FOR CARRYING OUT THE INVENTION

20 In a constitution wherein titanium oxide layers and metal layers are alternately laminated, when the number of lamination is increased, the wavelength width in which a low reflectance can be obtained in the visible light region will increase. However, it was confirmed that the
25 tendency of decrease in transmittance becomes significant along with increase in the number of lamination, more than expected from optical interference effect. The

present inventors have conducted extensive studies on this phenomenon and as a result, found that the decrease in transmittance occurs at the interface between the titanium oxide layer and the metal layer. This phenomenon is estimated to be light absorption due to surface plasmon excited by light irradiation in the inside of the metal layer, particularly in the vicinity of the interface with the titanium oxide layer, and it is considered that formation of the surface plasmon can be suppressed to reduce the decrease in transmittance by interposing a layer having a refractive index lower than that of the titanium oxide as an interlayer.

In the laminate of the present invention, on a first titanium oxide layer on the substrate side, a metal layer and a titanium oxide layer are laminated alternately in pairs. One pair of the metal layer and the titanium oxide layer may be laminated, or a plural pairs may be laminated. For example, the laminate of the present invention may have a layer constitution wherein on a first layer, a metal layer and a titanium oxide layer each in a single layer may be laminated, or may have a layer constitution wherein on a first layer, plurality of metal layers and titanium oxide layers are alternately laminated one on another in this order.

With respect to the laminate of the present invention, the substrate is not particularly limited, and it may, for example, be 1) glass for window made of e.g.

soda lime glass, wire glass or frost glass, 2) window glass for vehicles such as automobiles, 3) plastic films of e.g. PET, 4) plastic sheets made of e.g. an acrylic resin, or 5) glass, plastic films and plastic sheets to
5 be used for display. Particularly preferred is a transparent substrate.

Each of the titanium oxide layers in the laminate of the present invention is preferably a layer having a refractive index of at least 2.4 as a wavelength of 550
10 nm, and may be one consisting of an oxide of titanium (titania) alone or may contain a small amount of another element component other than titanium. As another element component, Nb, Cr or Zr may, for example, be mentioned.

15 The thickness (geometrical film thickness, the same applies hereinafter) of the first layer on the substrate side and the titanium oxide layer which is located at the furthest from the substrate is preferably from 20 to 60 nm, particularly preferably from 25 to 45 nm. The
20 thickness of the titanium oxide layer other than the first layer and the titanium oxide layer which is located at the furthest from the substrate is preferably from 40 to 120 nm, particularly preferably from 50 to 90 nm. Further, the first layer and the titanium oxide layer
25 which is located at the furthest from the substrate have a thinner film thickness (particularly a thickness at a level of $1/2$) than another titanium oxide layer from the

viewpoint to decrease the visible light reflectance and to increase the wavelength range in which a low reflectance can be obtained.

In the laminate of the present invention, the
5 plurality of titanium oxide layers may have the same composition or may have different compositions.

In the laminate of the present invention, the metal layer is preferably a layer containing at least one metal selected from the group consisting of silver, copper and
10 gold. It may be silver, copper, gold or an alloy containing them as the main component.

Specific examples of an alloy containing silver, copper or gold as the main component include 1) a silver-Pd alloy containing Pd in an amount of at most 5.0
15 atomic% (preferably within a range of from 0.1 to 3 atomic%), 2) a silver-gold alloy containing Au in an amount of at most 5.0 atomic% (preferably within a range of from 0.1 to 3 atomic%), and 3) a silver-Pd-Cu alloy containing Pd and Cu each in an amount of from 0.5 to 3
20 atomic%. Here, the above inclusion proportion is a proportion based on the total amount including silver, and the same applies hereinafter.

In a case where the laminate of the present invention has a plurality of metal layers, the metal
25 layers may be layers having the same composition or may be layers having different compositions.

The thickness of the metal layer is preferably from

8 to 30 nm. The thickness of the metal layer which is closest to the substrate and the metal layer which is furthest from the substrate is preferably from 0.5 to 1.0 time the thickness of another metal layer from the viewpoint to decrease the visible light reflectance and to increase the wavelength range in which a low reflectance can be obtained.

Further, in the case where the laminate of the present invention has a plurality of metal layers, the total of the thicknesses (thickness of the plurality of metal layers) is preferably at most 120 nm.

From the viewpoint to decrease the visible light reflectance and to increase the wavelength range in which a low reflectance can be obtained, the number of metal layers is preferably two in a case where the targeted resistance value of the laminate to be obtained is $2.5 \Omega/\square$, it is preferably three in a case where the targeted resistance value is $1.5 \Omega/\square$, and it is preferably four in a case where the targeted resistance value is $0.5 \Omega/\square$.

In the laminate of the present invention, a plurality of interlayers may be interposed, and they may be provided on and below the metal layer so that the metal layer is sandwiched therebetween. Particularly preferred is such a constitution that all metal layers are sandwiched between two interlayers, whereby the highest visible light transmittance can be obtained.

Further, in the laminate of the present invention, a constitution wherein the interlayer is provided on the metal layer is preferred in view of excellence in abrasion resistance. In a case where an interlayer is provided on the metal layer which is furthest from the substrate in the laminate having a plurality of metal layers, the effect to improve the abrasion resistance tends to be significant as compared with a case where the interlayer is laminated on the metal layer which is closest to the substrate. Further, preferred is an interlayer consisting of at least one nitride selected from the group consisting of nitrides of boron, aluminum and silicon, from the viewpoint of abrasion resistance. Preferred is an interlayer consisting of a nitride of boron, aluminum or silicon, particularly silicon nitride (particularly SiN_x , $x=1.30$ to 1.36).

The interlayer may consist of any material so long as it is one having a refractive index of less than 2.4 at a wavelength of 550 nm. Particularly preferred is one made of a material having a refractive index of from 1.6 to 2.39. As the interlayer, preferred is a layer consisting of at least one member selected from the group consisting of an oxide, a nitride, an oxynitride, a carbide and a boride. Specific examples of the material constituting the interlayer include silicon nitride (refractive index: 2.0), niobium oxide (refractive index: 2.35), zinc oxide (refractive index: 2.0) and tin oxide

(refractive index: 2.0).

In the laminate of the present invention, the interlayer is not to improve the visible light transmittance due to optical interference effect, and it has an effect with a smaller thickness to cause the optical interference effect. The interlayer suppresses formation of the surface plasmon generated at the interface between the metal layer and the titanium oxide layer to suppress loss of visible light in the laminate generated due to light absorption by the surface plasmon.

Further, at the same time, the upper limit of the thickness of the interlayer (geometrical film thickness) is preferably 30 nm, particularly preferably 10 nm, furthermore preferably 5 nm from the viewpoint to decrease the visible light reflectance and to increase the wavelength range in which a low reflectance can be obtained.

From the viewpoint of abrasion resistance, the upper limit of the thickness of the interlayer is preferably 20 nm, particularly preferably 15 nm.

The lower limit of the thickness of the interlayer is preferably 0.1 nm, particularly preferably 0.5 nm.

In a case where there are a plurality of interlayers, the total of the thicknesses (the thickness of the plurality of interlayers) is preferably at most 40 nm.

With respect to the effect to improve the visible

light transmittance relative to the number of interlayers, an additive law is substantially confirmed.

The laminate of the present invention has a high electrical conductivity, and it thereby has an electromagnetic wave shielding property. Further, it has a high reflectance in the near infrared region, it thereby has a near-infrared shielding property also. For example, the transmittance at a wavelength of 900 nm is preferably at most 15%.

With respect to the laminate of the present invention, it is preferred that the sheet resistance value is from 0.5 to 3.5 Ω/\square , the visible light transmittance is at least 40%, and the visible light reflectance is at most 10%.

Further, the laminate of the present invention preferably has an emissivity of at most 0.08.

It is also preferred to use the laminate of the present invention with a purpose of suppressing leakage of electromagnetic wave radiating from an electromagnetic wave release source such as a plasma display.

The laminate of the present invention has an electromagnetic wave shield factor at 30 MHz of preferably at least 10 db, particularly preferably at least 15 db, furthermore preferably at least 17 db. When the sheet resistance value is the same, the electromagnetic shield factor is substantially the same.

Further, when the laminate of the present invention

is used in an application wherein importance is attached to a low-reflecting property, it is preferred to further laminate a resin film having a low-reflecting property on the laminate, whereby the visible light reflectance can
5 be made to be at most 3%.

Further, when the laminate of the present invention is used in an application wherein importance is attached to a near-infrared shielding property, it is preferred to further laminate a resin film having a near-infrared
10 shielding property, whereby the transmittance at a wavelength of 900 nm can be made to be at most 5%.

The resin film is attached 1) on the multilayer film of the laminate of the present invention and/or 2) on the substrate surface on the side opposite to the substrate
15 surface on which the laminate of the present invention is formed thereon.

As the resin film having a low-reflecting property, one having an antireflection layer formed on a resin film made of e.g. urethane or PET may be mentioned. Said
20 resin film has a shatterproof property together with the low-reflecting property. As the antireflection layer, 1) a low-refractive index layer consisting of an amorphous fluorine-containing polymer (such as Cytop, manufactured by Asahi Glass Company, Limited), 2) a low-refractive
25 index layer made of e.g. SiO_2 or MgF_2 , 3) a multilayer film having low-refractive index layers and high-refractive index layers alternately overlaid one on

another, or 4) a porous silica layer may, for example, be mentioned.

As the resin film having a near-infrared shielding property, one having a near-infrared absorbent mixed in a resin film made of e.g. urethane or PET may be mentioned. Further, a near-infrared absorbent may be mixed in an adhesive layer to be used for attachment.

In production of the laminate of the present invention, formation of the titanium oxide layer may be carried out, for example, in accordance with a method of forming it by means of a direct-current sputtering method by using a reducing target of a titanium oxide, a reactive sputtering method, an ion plating method, a vapor deposition method or a CVD method. Among them, the method of forming it by means of a direct-current sputtering method by using a reducing target of a titanium oxide is favorable since oxidation of the metal layer can be prevented when the titanium oxide layer is formed on the metal layer, and a uniform formation can be carried out at a high speed in a large area. Oxidation of the metal layer can be prevented, with the result that the obtained laminate has an improved visible light transmittance and a decreased emissivity.

The reducing target of a titanium oxide is a target having deficient oxygen relative to a stoichiometric composition of the titanium oxide. Specifically, it is preferred to use one having a composition represented by

the formula TiO_x ($1 < x < 2$). The reducing target of a titanium oxide may be produced, for example, by a high pressure compression method, a sintering method or a flame spray coating method using a titania powder or a mixture of a titania powder with a titanium powder as a material, as disclosed in International Publication WO97/08359.

In a case of using a reducing target, it is preferred to use, as a sputtering gas, an inert gas containing from 0.1 to 10 vol% of an oxidizing gas. Use of an inert gas containing an oxidizing gas at a concentration within this range as a sputtering gas is effective to suppress oxidation of the metal layer when the titanium oxide layer is formed, and is effective to produce a laminate having a low emissivity and a high electrical conductivity. It is particularly preferred to use an inert gas containing from 0.1 to 5 vol% of an oxidizing gas.

As the oxidizing gas, oxygen gas may commonly be used, and e.g. nitrogen monoxide, nitrogen dioxide, carbon monoxide, carbon dioxide or ozone may be used.

Formation of the metal layer can be carried out in accordance with e.g. a sputtering method, a CVD method or a vapor deposition method. Particularly preferred is formation by a direct-current sputtering method since the film-formation rate is high, and a layer having a uniform quality can be formed in a uniform thickness in a large

area.

Formation of the interlayer can be carried out in accordance with a method properly selected depending on the composition of the layer to be formed. For example,
 5 it may be carried out by e.g. a sputtering method, a CVD method or a vapor deposition method. Particularly preferred is a direct-current sputtering method.

The laminate of the present invention can be used for heat shielding articles (such as heat shielding
 10 window glass), optical filters (such as near-infrared shielding filters to be disposed in front of PDP), electromagnetic wave shielding articles (such as electromagnetic wave shielding plate to be disposed in front of PDP), low-reflecting articles (such as low-
 15 reflecting window glass and low-reflecting displays), heat ray-reflecting plates and transparent electrodes.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples and Comparative
 20 Examples. In the following Examples and Comparative Examples, measurement of the visible light transmittance and emissivity and evaluation of the abrasion resistance were carried out in accordance with the following methods.

25 Measurement of visible light transmittance and visible light reflectance

The spectral transmittance and the spectral

reflectance at a wavelength of from 340 to 780 nm were measured, and the visible light transmittance and the visible light reflectance were obtained by the relative luminous efficiency of CIE light adaptation relative to CIE standard light D₆₅ as specified in JIS Z8720, in accordance with JIS R3106.

Measurement of emissivity

In accordance with JIS R3106, with respect to a standard sample of which the hemisphere emissivity was preliminarily obtained, the emissiometer value was measured by SCALING DIGITAL VOLTMETER (common name: emissiometer) manufactured by Devices & Services, and the conversion factor between the hemisphere emissivity and the emissiometer value was preliminarily obtained.

With respect to samples obtained in Examples and Comparative Examples, the emissiometer value was measured, and the emissiometer value was multiplied by the above conversion factor to obtain the hemisphere emissivity.

Evaluation of abrasion resistance

In accordance with JIS K5400, a scratch value by pencil with a load of 1 kg was measured, and employed as an index of the abrasion resistance.

EXAMPLE 1

Using a target (area: 432 mm × 127 mm) consisting of TiO_x (x=1.94), a titania layer (refractive index: 2.45) having a thickness of 33 nm was formed on the surface of

a soda lime glass, with an application electric power of 4 kw by using argon gas containing 2 vol% of oxygen as a sputtering gas. Here, the proportion of oxygen is a proportion based on the entire sputtering gas, and the same applies hereinafter.

On the titania layer, a metal layer consisting of silver containing 1 atomic% of Pd (hereinafter referred to simply as "Ag-1 at% Pd layer") (thickness: 14 nm) was formed by using a target (area: 432 mm × 127 mm) consisting of silver containing 1 atomic% of palladium by using argon gas as a sputtering gas by applying an electric power of 0.3 kw. Here, the proportion of palladium in the target is a proportion based on the total amount with silver, and the same applies hereinafter.

Further, on the Ag-1 at% Pd layer, an interlayer consisting of silicon nitride (SiN_x , $x=1.34$) (hereinafter referred to as " SiN_x interlayer") (refractive index: 1.95, thickness: 0.5 nm) was formed by using Si (area: 432 mm × 127 mm) as a target, by using argon gas containing 30 vol% of nitrogen as a sputtering gas with an application electric power of 1 kW. Then, on the interlayer, a titania layer having a thickness of 33 nm was formed in the same manner as mentioned above to obtain a laminate A-1. Here, a laminate obtained in Example X will be referred to as "laminate A-X" below.

The obtained laminate A-1 has a constitution wherein

on a soda lime glass 1, a titania layer 2_1 , a Ag-1 at% Pd layer 3_1 , a SiN_x interlayer 4_{12} and a titania layer 5_1 sequentially laminated, as illustrated in Fig. 1.

In Figures, 1 designates a soda lime glass, 2_1 designates a titania layer, 3_1 , 3_2 , 3_3 and 3_4 designate a Ag-1 at% Pd layer, 4_{11} , 4_{12} , 4_{21} , 4_{22} , 4_{31} , 4_{32} , 4_{41} and 4_{42} designate an interlayer, 5_1 , 5_2 , 5_3 and 5_4 designate a titania layer, 6 designates a top coat layer, 7 designates a bottom coat layer and 8 designates a resin film.

Of the laminate A-1, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity are shown in Table 1.

COMPARATIVE EXAMPLE 1

A laminate B-1 having a constitution wherein on a soda lime glass 1, a titania layer 2_1 having a thickness of 33 nm, a Ag-1 at% Pd layer 3_1 having a thickness of 14 nm and a titania layer 5_1 having a thickness of 33 nm were formed, as illustrated in Fig. 2, was obtained in the same manner as in Example 1 except that no SiN_x interlayer 4_{12} was formed. Here, a laminate obtained in Comparative Example Y will be referred to as "laminate B-Y" below.

Of the obtained laminate B-1, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity are shown in Table 1.

EXAMPLES 2 to 17 and COMPARATIVE EXAMPLES 2 to 5

Laminates A-2 to A-17 and laminates B-2 to B-5 were produced in the same manner as in Example 1 by changing the thickness of the SiN_x interlayer within a range of from 0.5 to 5 nm and by changing the position to which
5 the interlayer was formed, as identified in Tables 1 and 2.

The laminates A-2 to A-5 (Examples 2 to 5) have a constitution wherein on a soda lime glass 1, a titania layer 2_1 , a Ag-1 at% Pd layer 3_1 , a SiN_x interlayer 4_1 and
10 a titania layer 5_1 were sequentially laminated, as illustrated in Fig. 1.

The laminates A-6 to A-12 (Examples 6 to 12) have a constitution wherein on a soda lime glass 1, a titania layer 2_1 , a SiN_x interlayer 4_{11} , a Ag-1 at% Pd layer 3_1
15 and a titania layer 5_1 were sequentially laminated, as illustrated in Fig. 3.

The laminates A-13 to A-17 (Examples 13 to 17) have a constitution wherein on a soda lime glass 1, a titania layer 2_1 , a SiN_x interlayer 4_{11} , a Ag-1 at% Pd layer 3_1 , a
20 SiN_x interlayer 4_{12} and a titania layer 5_1 were sequentially laminated, as illustrated in Fig. 4.

The laminates B-2 and B-3 (Comparative Examples 2 and 3) have a constitution wherein on a soda lime glass 1, a titania layer 2_1 , a Ag-1 at% Pd layer 3_1 , a titania
25 layer 5_1 and a top coat layer 6 consisting of SiN_x were sequentially laminated, as illustrated in Fig. 5.

The laminates B-4 and B-5 (Comparative Examples 4

and 5) have a constitution wherein on a soda lime glass 1, a bottom coat layer 7 consisting of SiN_x , a titania layer 2₁, a Ag-1 at% Pd layer 3₁ and a titania layer 5₁ were sequentially laminated, as illustrated in Fig. 6.

5 Here, each of the top coat layer consisting of SiN_x and the bottom coat layer consisting of SiN_x was formed by the same formation method of the SiN_x interlayer.

With respect to the obtained laminates A-2 to A-17 and the laminates B-2 to B-5, the visible light
10 transmittance, the visible light reflectance, the sheet resistance value and the emissivity were measured. The results are shown in Tables 1 and 2.

Further, the relation between the thicknesses of the interlayers and the visible light transmittances of the
15 laminates A-1 to A-17 are illustrated in Fig. 7. In Fig. 7, the laminates A-1 to A-5 having the SiN_x interlayer 4₁₂ on the Ag-1 at% Pd layer 3₁ are represented by ●, the laminates A-6 to A-12 having the SiN_x interlayer 4₁₁ below the Ag-1 at% Pd layer 3₁ are represented by ■, and the
20 laminates A-13 to A-17 having the SiN_x interlayers 4₁₁ and 4₁₂ on and below the Ag-1 at% Pd layer 3₁ are represented by ▲.

Further, the visible spectral characteristics of the laminates A-1 and A-2 are shown in Fig. 8 together with
25 the visible spectral characteristics of the laminate B-1.

Still further, the visible spectral characteristics of the laminates A-6 and A-8 are shown in Fig. 9 together

with the visible spectral characteristics of the laminate B-1.

Further, the visible spectral characteristics of the laminates A-13, A-14 and A-15 are shown in Fig. 10

5 together with the visible spectral characteristics of the laminate B-1.

As evident from the results shown in Table 1 and Fig. 7, the laminates having a constitution wherein SiN_x interlayers are formed on and below the Ag-1 at% Pd layer, show a higher visible light transmittance than the laminate having a constitution wherein an interlayer is formed only on or below the Ag-1 at% Pd layer, and show a visible light transmittance higher by about 3% as compared with the laminate B-1 having a constitution with
10 no interlayer of Comparative Example 1. The effect can be obtained with a film thickness of the SiN_x interlayer of 0.5 nm, and the effect does not depend on the film thickness. The bottom coat of SiN_x before film formation of the first titania layer and the top coat of SiN_x as
15 the outermost layer have substantially no effect to improve the transmittance.

EXAMPLES 18 to 21

Laminates A-18 to A-21 were produced in the same manner as in Example 1 except that the thickness or the
25 position of the SiN_x interlayer was changed as identified in Table 3.

With respect to the obtained laminates A-18 to 21,

the abrasion resistance was evaluated. Further, the laminates obtained in Examples 1, 2, 4, 5, 8, 11 and 12 and Comparative Example 1 were also evaluated similarly. The results are shown in Table 3.

5 It is found from the results as shown in Table 3 that of the laminates having a layer constitution wherein a SiN_x interlayer having a thickness of at least 0.5 nm was formed on the Ag-1 at% Pd layer, the pencil scratch value as an index of the abrasion resistance is improved.

10 Further, it is found that of the laminates having a layer constitution wherein a SiN_x interlayer having a thickness of at least 1 nm was formed below the Ag-1 at% Pd layer, the pencil scratch value as an index of the abrasion resistance is improved. Further, it is found that the

15 laminates having a layer constitution wherein an interlayer is formed on the Ag-1 at% Pd layer have a greater effect to improve the pencil scratch value, and the pencil scratch value is further improved by increasing the thickness of the interlayer.

20 EXAMPLE 22

 In the same manner as in Example 1, a laminate A-22 having a constitution as illustrated in Fig. 11 was produced by sequentially laminating, on a soda lime glass 1, a titania layer 2_1 having a thickness of 33 nm, a SiN_x

25 interlayer 4_{11} having a thickness of 1 nm, a Ag-1 at% Pd layer 3_1 having a thickness of 14 nm and a titania layer 5_1 having a thickness of 66 nm, and further laminating a

Ag-1 at% Pd layer 3₂ having a thickness of 14 nm and a titania layer 5₂ having a thickness of 33 nm.

Of the obtained laminate A-22, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity are shown in Table 4 (No. 1).

COMPARATIVE EXAMPLE 6

A laminate B-6 having a constitution as illustrated in Fig. 12 was produced in the same manner as in Example 22 except that no interlayer 4₁₁ was formed.

Of the obtained laminate B-6, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity are shown in Table 4.

EXAMPLES 23 to 44

Laminates A-23 to A-40 were produced in the same manner as in Example 22 except that the thickness or the position of the SiN_x interlayer was changed as identified in Table 4 (Nos. 1 and 2).

The laminate A-23 (Example 23) has a constitution as illustrated in Fig. 11, the laminates A-24 and A-25 (Examples 24 and 25) in Fig. 13, the laminates A-26 and A-27 in Fig. 14, the laminates A-28 and A-29 in Fig. 15, the laminates A-30 and A-31 in Fig. 16, the laminates A-32 and A-33 in Fig. 17, the laminates A-34 and A-35 in Fig. 18, the laminates A-36 and A-37 in Fig. 19 and the laminates A-38 to A-40 in Fig. 20, respectively.

With respect to the laminates A-23 to A-40, the

visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity are measured. They are shown in Table 4 (Nos. 1 and 2) together with the results of the laminate B-6.

5 Further, the visible spectral characteristics of the laminates A-38, A-39 and A-40 are shown in Fig. 21 together with the visible spectral characteristics of the laminates B-6. Here, the sheet resistance value was measured before a low-reflection resin film was attached.

10 The same applies hereinafter.

The laminates having a SiN_x interlayer formed on and below the two Ag-1 at% Pd layers show the highest visible light transmittance, and show a visible light transmittance higher by about 6% as compared with the
15 laminate having no SiN_x interlayer formed of Comparative Example 6. The effect can be obtained with a film thickness of the SiN_x interlayer of 1 nm, and the effect does not depend on the film thickness.

In order to obtain a laminate having a sheet
20 resistance value of $2.5 \Omega/\square$ and a visible light transmittance of at least 74%, it is preferred to form a SiN_x interlayer on and below a Ag-1 at% Pd layer, and preferred is a laminate wherein the $(2n + 1)$ layers are five layers.

25 Further, with respect to the laminate A-38, the transmittance of light having a wavelength of 900 nm and the electromagnetic wave shield factor at a frequency of

30 MHz were measured, and they were 14.5% and 15 dB, respectively. From these results, it is found that the laminate A-38 has good near-infrared shielding property and electromagnetic wave shielding property.

5 EXAMPLES 38a, 39a and 40a

Laminates A-38a, A-39a and A-40a were produced in the same manner as in Examples 38, 39 and 40, respectively, except that metal layers made of silver containing 1 atomic% each of Pd and Cu (hereinafter referred to simply as "Ag-1 at% Pd-1 at% Cu layer") were formed by using a target (area: 432 mm × 127 mm) consisting of silver containing 1 atomic% of palladium and 1 atomic% of copper by using argon gas as a sputtering gas by charging an electric power of 0.3 kw, instead of the Ag-1 at% Pd layers formed by using the target (area: 432 mm × 127 mm) consisting of silver containing 1 atomic% of palladium. The obtained laminates were evaluated in the same manner as the laminate A-38. The results are shown in Table 4 (No. 3).

20 COMPARATIVE EXAMPLE 6a

A laminate was obtained in the same manner as the laminate A-38a of Example 38a except that no interlayer was formed, and the obtained laminate was evaluated in the same manner as the laminate A-38. The results are shown in Table 4 (No. 3).

With the laminates using Ag-1 at% Pd-1 at% Cu layers, the same good results can be obtained as the

laminate using Ag-1 at% Pd layers.

Further, it was confirmed that humidity resistance was improved due to the synergistic effect of the two types of metals (Pd and Cu) contained in silver, as
5 compared with the case where one type of metal is contained.

EXAMPLES 38b, 39b and 40b

Laminates A-38b, A-39b and A-40b were produced in the same manner as in Examples 38, 39 and 40,
10 respectively, except that metal layers consisting of silver containing 1 atomic% of Au (hereinafter referred to simply as "Ag-1 at% Au layer") were formed by using a target (area: 432 mm × 127 mm) consisting of silver containing 1 atomic% of gold by using argon gas as a
15 sputtering gas by charging an electric power of 0.3 kw, instead of the Ag-1 at% Pd layers formed by using the target (area: 432 mm × 127 mm) consisting of silver containing 1 atomic% of palladium. The obtained laminates were evaluated in the same manner as the
20 laminate A-38. The results are shown in Table 4 (No. 4).

COMPARATIVE EXAMPLE 6b

A laminate was produced in the same manner as the laminate A-38b of Example 38b except that no interlayer was formed, and the obtained laminate was evaluated in
25 the same manner as the laminate A-38. The results are shown in Table 4 (No. 4).

With the laminates using Ag-1 at% Au layers, the

same good results can be obtained as the laminate using Ag-1 at% Pd layers. Further, with the laminate using Ag-1 at% Au layers, a visible light transmittance higher by about 2% as compared with the laminate using Ag-1 at% Pd layers can be obtained, and at the same time, a sheet resistance value lower by about 10% can be obtained when a film thickness of the metal layer is at the same level.

EXAMPLE 41

A resin film having a low-reflecting property, comprising a polyurethane type soft resin film (thickness: 200 μm), and a low-refractive index antireflection layer consisting of an amorphous fluorine-containing polymer (Cytop, manufactured by Asahi Glass Company, Limited) formed on one side of said resin film and an acrylic type adhesive layer formed on the other surface of the resin film (hereinafter referred to as "low-reflecting resin film") was prepared.

Then, as illustrated in Fig. 22, the low-reflecting resin film 8 was attached on the titania layer 52 of the laminate A-38 obtained in Example 38 and on the surface of the soda lime glass on the side opposite to the side on which the laminate layers were laminated, to produce a laminate A-41.

Of the obtained laminate A-41, the visible light transmittance, the visible light reflectance, the transmittance of light having a wavelength of 900 nm and the sheet resistance value were measured in the same

manner as in Example 38. The results are shown in Table 5.

EXAMPLE 42

In the acrylic type adhesive layer of the low-reflecting resin film used in Example 41, a near-infrared absorbent (SIR 159, manufactured by Mitsui Chemicals Inc.) was added in an amount of 5 wt% based on the acrylic type adhesive, to prepare a resin film having a near-infrared shielding property imparted together with a low-reflecting property (hereinafter referred to as "low-reflecting near-infrared shielding resin film").

Then, in the same manner as in Example 41, the low-reflecting near-infrared shielding resin film was attached on the titania layer 52 of the laminate A-38 obtained in Example 38 and on the surface of the soda lime glass on the side opposite to the side on which the laminated layers were laminated to produce a laminate A-42. The obtained laminate A-42 was measured in the same manner as in Example 38. The results are shown in Table 5.

It is found from the results as shown in Table 5 that by attaching low-reflecting resin films, the visible light reflectance can be suppressed to be less than 2% while obtaining a visible light transmittance of at least 74%, and a better low-reflecting property than the laminate A-38 can be obtained. Further, it is found that by attaching low-reflecting near-infrared shielding resin

films, the transmittance of light having a wavelength of 900 nm can be suppressed to be at most 5% substantially without impairing good optical characteristics at the visible light region, and a still better near-infrared shielding property than the laminate A-38 can be obtained.

Further, with respect to the laminates A-24, 25, 28, 29, 32 and 33 and the laminate B-6, the abrasion resistance was evaluated and the results are shown in Table 6.

It is found from the results as shown in Table 6 that the laminate having a plurality of Ag-1 at% Pd layers wherein an interlayer is formed on the outermost Ag-1 at% Pd layer a greater effect to improve the abrasion resistance as compared with a case where an interlayer is laminated on the lower Ag-1 at% Pd layer. Further, it is preferred to form an interlayer on each of the plurality of the Ag-1 at% Pd layers.

EXAMPLE 43

A laminate A-43 having a layer constitution as illustrated in Fig. 23, each layer having a constitution as identified in Table 7, was produced.

Of the obtained laminate A-43, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 7.

COMPARATIVE EXAMPLE 7

A laminate B-7 having a layer constitution as

illustrated in Fig. 24, each layer having a constitution as identified in Table 7, was produced in the same manner as in Example 43 except that no interlayer was formed.

Of the obtained laminate B-7, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 7.

EXAMPLES 44 and 45

Laminates A-44 and 45 having layer constitutions as illustrated in Fig. 25 (Example 44) and Fig. 26 (Example 45), respectively, each layer having a constitution as identified in Table 7, were produced in the manner as in Example 43.

Of the obtained laminates A-44 and 45, the visible light transmittance, the visible light reflectance and the sheet resistance value were measured, and the results are shown in Table 7 together with the results in Example 43.

It is found from the results as shown in Table 7 that preferred is a laminate having a SiN_x interlayer formed on and below the Ag-1 at% Pd layers and wherein the $(2n + 1)$ layers are seven layers, in order to obtain a laminate having a sheet resistance value of $1.5 \Omega/\square$ and a visible light transmittance of at least 67%.

Further, with respect to the laminate A-45, the transmittance of light having a wavelength of 900 nm and the electromagnetic wave shield factor at a frequency of 30 MHz were measured, and they were 2.4% and 17 dB,

respectively, and the laminate was found to have good near-infrared shielding property and electromagnetic wave shielding property.

EXAMPLE 46

5 A laminate A-46 was produced by attaching a low-reflecting resin film 8 on the titania layer 53 of the laminate A-45 obtained in Example 45 and on the surface of the soda lime glass on the side opposite to the side on which the laminated layers were laminated, as
10 illustrated in Fig. 27.

Of the obtained laminate A-46, the visible light transmittance, the visible light reflectance, the sheet resistance value and the transmittance of light having a wavelength of 900 nm are shown in Table 8.

15 EXAMPLE 47

A laminate A-47 was produced in the same manner as in Example 46 by attaching a low-reflecting near-infrared shielding resin film on the titania layer 5₃ of the laminate A-45 obtained in Example 45 and on the surface
20 of the soda lime glass on the side opposite to the side on which the laminated layers were laminated. With respect to the obtained laminate A-47, measurement was carried out in the same manner as in Example 46. The results are shown in Table 8.

25 As shown in Table 8, it is found that by attaching low-reflecting resin films, the visible light reflectance can be suppressed to be less than 2% while obtaining a

visible light transmittance of at least 67%, and a still better low-reflecting property than the laminate A-45 can be obtained. Further, it is found that by attaching low-reflecting near-infrared shielding resin films, a still
5 better near-infrared shielding property than the laminate A-45 can be obtained substantially without impairing good optical characteristics at the visible light region.

EXAMPLE 48

A laminate A-48 having a layer constitution as
10 illustrated in Fig. 28, each layer having a constitution as identified in Table 9, was produced.

Of the obtained laminate A-48, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 9.

15 COMPARATIVE EXAMPLE 9

A laminate B-9 having a layer constitution as illustrated in Fig. 29, each layer having a constitution as identified in Table 9, was produced in the same manner as in Example 48 except that no interlayer was formed.

20 Of the obtained laminate B-9, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 9.

EXAMPLES 49 to 54 and COMPARATIVE EXAMPLES 10 and 11

Laminates A-49 to A-54 were produced in the same
25 manner as in Example 48 except that the thickness of the titania layer, the SiN_x interlayer or the Ag-1 at% Pd layer was changed as identified in Table 9. Further,

laminates B-10 and B-11 were produced in the same manner as in Comparative Example 9 except that the thickness of the titania layer or the Ag-1 at% Pd layer was changed as identified in Table 9.

5 Of the obtained laminates A-49 to A-54 and the laminates B-10 and B-11, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 9.

10 The laminates having a constitution wherein the SiN_x interlayer is formed on and below the Ag-1 at% Pd layers show a high visible light transmittance and show a transmittance higher by about 15% than the laminates having no interlayer of Comparative Examples 9 to 11. Further, the effect can be obtained with a film thickness
15 of the SiN_x interlayer of 1 nm, and the effect does not depend on the film thickness of the SiN_x interlayer.

20 With respect to Examples 48 to 50 and Comparative Examples 9 to 11, the relation between the visible light transmittance and the sheet resistance value is shown in Fig. 30, and the relation between the visible light reflectance and the sheet resistance value is shown in Fig. 31.

25 It is found from the results shown in Figs. 30 and 31 that preferred is a laminate having a SiN_x interlayer formed on and below the Ag-1 at% Pd layers and wherein the $(2n + 1)$ layers are nine layers as in Examples 48 to 50, in order to obtain a laminate having a visible light

transmittance of at least 40% and a visible light reflectance of at most 10% together with a low sheet resistance value of from 0.5 to 0.9 Ω/\square . Here, the electromagnetic wave shield factor showed a value exceeding 17 db (about 20 db or above) in each Example.

EXAMPLE 55

A laminate A-55 was produced by attaching a low-reflecting resin film 8 on the titania layer 5₄ of the laminate A-48 obtained in Example 48 and on the surface of the soda lime glass on the side opposite to the side on which the laminated layers were laminated, as illustrated in Fig. 32.

Of the obtained laminate A-55, the visible light transmittance and the visible light reflectance are shown in Table 10.

EXAMPLES 56 and 57

Laminates A-56 and 57 were produced in the same manner as in Example 55 by attaching a low-reflecting resin film 8 on the titania layer 5₄ of the laminates A-49 and 50 obtained in Examples 49 and 50 and on the surface of the soda lime glass on the side opposite to the side on which the laminated layers were laminated.

COMPARATIVE EXAMPLES 12 to 14

Laminates B-12 to 14 were produced in the same manner as in Example 55 by attaching a low-reflecting resin film on the titania layer 5₄ of the laminates B-9 to 11 of Comparative Examples 9 to 11 and on the surface

of the soda lime glass on the side opposite to the side on which the laminated layers were laminated.

Of the obtained laminates A-55 to A-57 and laminates B-12 to B-14, the visible light transmittance, the visible light reflectance and the sheet resistance value are shown in Table 10. Here, the sheet resistance value was measured before the attachment of the low-reflecting resin films.

With respect to Examples 55 to 57 and Comparative Examples 12 to 14, the relation between the visible light transmittance and the sheet resistance value is shown in Fig. 33, and the relation between the visible light reflectance and the sheet resistance value is shown in Fig. 34. It is found from the results shown in Figs. 33 and 34 that a layer constitution wherein four layers each of the Ag-1 at% Pd layers and the titanium oxide layers were alternately laminated with the SiN_x interlayer interposed therebetween and the low-reflecting resin film was attached on the titania layer 54 and on the soda lime glass substrate, is preferred in order to obtain a laminate having a visible light transmittance of at least 40% and a visible light reflectance of at most 3% together with a low sheet resistance value of from 0.5 to 0.9 Ω/\square .

EXAMPLES 58 to 62

Laminates A-58 to A-62 were produced in the same manner as in Examples 13 to 17 except that formation of

each titania layer was carried out by using a Ti target (area: 432 mm × 127 mm) with an application electric power of 4 kW by using argon gas containing 50 vol% of oxygen gas as a sputtering gas, and the thickness of the
5 SiN_x interlayer was from 1.0 to 3.0 nm.

COMPARATIVE EXAMPLE 15

A laminate B-15 was produced in the same manner as in Comparative Example 1 except that formation of the titania layer was carried out by using a Ti target (area:
10 432 mm × 127 mm) with an application electric power of 4 kW by using argon gas containing 50 vol% of oxygen gas as a sputtering gas.

COMPARATIVE EXAMPLE 16

A laminate B-16 was produced in the same manner as
15 in Comparative Example 15 except that after the Ag-1 at% Pd layer was formed, a Ti layer of 1.5 nm was formed by using a Ti target (area: 432 mm × 127 mm) with an application electric power of 1 kW by using argon gas as a sputtering gas.

20 Of the laminates A-58 and 62 and the laminates B-15 to 16 obtained in Examples 58 to 62 and Comparative Examples 15 to 16, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity were measured. The results of Examples 58
25 to 62 are shown in Table 11, and the results of Comparative Examples 15 to 16 are shown in Table 12.

In a case of forming a titania layer by conventional

reactive sputtering by using a Ti target, it is necessary to carry out film formation by using a sputtering gas containing an oxidizing gas in a large amount. In this case, oxygen negative ions are formed in a large amount
5 due to impact of the oxidizing gas and electron, and the generation probability reaches from 20 to 30% in a case of impact on electron having a kinetic energy of several tens eV. The oxygen negative ions thus formed in a large amount are accelerated in the substrate direction by an
10 electric field in the vicinity of the target charged negatively. The accelerated oxygen negative ions have a kinetic energy at a level of from 100 to 200 eV in the vicinity of the substrate, and are impacted in the Ag-1 at% Pd layer which is a layer under the titania layer in
15 a depth at a level of 1.5 nm on the average to oxidize the metals. Due to this oxidization, the sheet resistance value and the emissivity tend to increase, whereby an electrically conductive laminate (low-emissive laminate) tends to hardly be obtained.

20 With respect to the laminate B-15 obtained in Comparative Example 15, the metals in the Ag-1 at% Pd layer were oxidized in process of forming the titania layer, whereby the resistance value and the emissivity increased, and no electrical conductivity and low-
25 emissivity were obtained.

The laminate B-16 obtained in Comparative Example 16 has a constitution wherein a titania layer was laminated

on the Ag-1 at% Pd layer with a Ti layer interposed therebetween. Oxidation of the Ag-1 at% Pd layer under the titania layer, due to impact of the oxygen negative ions in process of forming the titania layer, was
5 prevented by providing a Ti layer.

In a case where the thickness of the Ti layer is at a level of 1.5 nm, substantially all the Ti layer after formation of the titania layer is oxidized to form a titania layer. Accordingly, the laminate B-16 obtained
10 finally has substantially the same layer constitution as the laminate B-1 having no interlayer obtained in Comparative Example 1.

It is found from the results shown in Tables 11 and 12 that with respect to the laminate having a titania
15 layer formed by a conventional reactive sputtering method by using a Ti target also, by interposing the SiN_x interlayer in an appropriate thickness (at least 2 nm) between the Ag-1 at% Pd layer and the titania layer, a high visible light transmittance can be obtained as
20 compared with the laminate B-16 having substantially no interlayer obtained in Comparative Example 16.

EXAMPLE 63

A laminate A-63 was obtained in the same manner as in Example 1 except that formation of the interlayer was
25 changed as follows.

Namely, on the Ag-1 at% Pd layer, an interlayer consisting of ZnO containing 5.7 wt% of Ga_2O_3

(hereinafter referred to simply as "GZO interlayer")
 (refractive index: 2.0, thickness: 0.5 nm) was formed by
 using a target (area: 432 mm × 127 mm) consisting of ZnO
 containing 5.7 wt% of Ga₂O₃ as calculated as Ga₂O₃ / (Ga₂O₃ +
 5 ZnO), by using argon gas as a sputtering gas with an
 application electric power of 1 kW.

The obtained laminate A-63 had a constitution
 wherein on a soda lime glass 1, a titania layer 2₁, a Ag-
 1 at% Pd layer 3₁, a GZO interlayer 4₁₂ and a titania
 10 layer 5₁ sequentially laminated, as illustrated in Fig.
 1. The thickness of each layer is shown in Table 13.
 EXAMPLES 64 to 80

Laminates A-64 to A-80 were produced in the same
 manner as in Example 63 except that the thickness or the
 15 position of the GZO interlayer was changed as identified
 in Table 13.

Of these laminates, the visible light transmittance,
 the visible light reflectance, the sheet resistance value
 and the emissivity were measured. The results are shown
 20 in Table 13.

Among the laminates having the GZO interlayer, one
 having an interlayer on and below the Ag-1 at% Pd layer
 disposed shows the highest visible light transmittance,
 and shows a visible light transmittance higher by about
 25 3% as compared with the case of interposing no interlayer
 of Comparative Example 1. The effect can be obtained
 with a film thickness of the GZO interlayer of 0.5 nm,

and the effect does not depend on the film thickness.

EXAMPLES 81 to 100

Laminates A-81 to A-100 were produced in the same manner as in Example 63 except that the thickness and the position of the GZO interlayer were changed as identified in Table 14, and the abrasion resistance was evaluated. The results are shown in Table 14 together with the results of Comparative Example 1.

It is found from the results shown in Table 14 that the laminate having a layer constitution wherein a GZO interlayer in a thickness of at least 1 nm was formed on or below the Ag-1 at% Pd layer, has an improved pencil scratch value as an index of the abrasion resistance. Further, it is found that the laminates having a layer constitution wherein an interlayer was formed on the Ag-1 at% Pd layer has a greater effect of improving the pencil scratch value, and that the pencil scratch value is further improved by increasing the thickness of the interlayer.

EXAMPLE 101

A laminate A-101 with a constitution having two Ag-1 at% Pd layers was produced in the same manner as in Example 22 except that the interlayer was changed into a GZO interlayer, by sequentially forming a titania layer of 33 nm, a GZO interlayer of 1 nm, a Ag-1 at% Pd layer of 14 nm, a titania layer of 66 nm, a Ag-1 at% Pd layer of 14 nm and a titania layer of 33 nm in this order on a

soda lime glass.

EXAMPLES 102 to 121

Laminates A-102 to A-121 were produced in the same manner as in Example 101 except that the thickness of the GZO interlayer or the position of the formation of the interlayer was changed, as identified in Table 15.

Of the obtained laminates A-101 to A-121, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity were measured. The results are shown in Table 15.

Among laminates having the GZO interlayer and having two Ag-1 at% Pd layers, a constitution wherein the GZO interlayer was disposed on and below both the first and second Ag-1 at% Pd layers shows the highest visible light transmittance, and shows a visible light transmittance higher by about 7% as compared with the case of interposing no interlayer of Comparative Example 6. The effect can be obtained with a film thickness of the GZO interlayer of 0.5 nm, and does not depend on the film thickness.

EXAMPLE 122

A laminate A-122 was obtained in the same manner as in Example 6 except that the interlayer was changed into the following layer consisting of NbO_x .

Namely, an interlayer consisting of NbO_x ($x=2.5$) (refractive index: 2.35, thickness: 0.5 nm) was formed by

using a target (area: 432 mm × 127 mm) consisting of NbO_x (x=2.49), by using argon gas containing 10 vol% of oxygen as a sputtering gas with an application electric power of 1 kW.

5 The obtained laminate A-122 has a constitution wherein on a soda lime glass 1, a titania layer, an interlayer consisting of NbO_x (hereinafter referred to as "NbO_x interlayer"), a Ag-1 at% Pd layer and a titania layer were sequentially laminated.

10 EXAMPLES 123 to 126

Laminates A-123 to A-126 were produced in the same manner as in Example 122 except that the thickness of the NbO_x interlayer was changed within a range of from 1 to 4 nm as identified in Table 16.

15 Of the obtained laminates A-122 to A-126, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity were measured. The results are shown in Table 16.

20 The laminate having the NbO_x interlayer below the Ag-1 at% Pd layer shows a visible light transmittance higher by about 1.5% as compared with Comparative Example 1 with no interlayer. Further, the effect can be obtained with a film thickness of the NbO_x interlayer of 0.5 nm, and
25 the effect does not depend on the film thickness.

EXAMPLE 127

A laminate A-127 was obtained in the same manner as

in Example 6 except that the interlayer was changed into the following layer consisting of SnO_2 containing indium.

An interlayer consisting of SnO_2 containing 10 wt% of indium (hereinafter referred to as "ITO interlayer")

5 (refractive index: 2.0, thickness: 1 nm) was formed by using a target (area: 432 mm \times 127 mm) consisting of SnO_2 containing 10 wt% of indium, by using argon gas as a sputtering gas with an application electric power of 1 kW.

10 EXAMPLES 128 to 131

Laminates A-128 to A-131 were produced in the same manner as in Example 127 except that the thickness of the ITO interlayer was changed within a range of from 1.5 to 4 nm as identified in Table 17.

15 Of the laminates A-127 to A-131, the visible light transmittance, the visible light reflectance, the sheet resistance value and the emissivity were measured. The results are shown in Table 17.

The laminates having the ITO interlayer below the
20 Ag-1 at% Pd layer shows a visible light transmittance higher by about 1.5% as compared with the laminate having no interlayer interposed of Comparative Example 1. The effect can be obtained with a film thickness of the ITO interlayer of 1 nm, and the effect does not depend on the
25 film thickness.

INDUSTRIAL APPLICABILITY

According to the present invention, a laminate by

using a titanium oxide, having an improved transmittance as the visible light region, can be obtained.

Further, according to the present invention, a laminate by using a titanium oxide, having an improved
5 abrasion resistance, can be obtained.

Table 1

(unit of layer thickness: nm)

	Comp. Ex.	Examples									
		1	2	3	4	5	6	7	8	9	10
7. Top coat (SiN _x)	-	-	-	-	-	-	-	-	-	-	-
6. Titania layer	33	33	33	33	33	33	33	33	33	33	33
5. SiN _x interlayer	-	0.5	1	2	3	5	-	-	-	-	-
4. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14
3. SiN _x interlayer	-	-	-	-	-	-	0.5	0.8	1	1.5	2
2. Titania layer	33	33	33	33	33	33	33	33	33	33	33
1. Bottom coat (SiN _x)	-	-	-	-	-	-	-	-	-	-	-
Visible light transmittance (%)	81.4	83.2	83	83.3	83.4	83.3	83.3	83.3	83.2	83.3	83.2
Visible light reflectance (%)	5.0	4.8	4.7	4.8	4.9	4.7	4.7	4.8	4.8	4.7	4.7
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	4.9	4.9	4.9	5.0	5.0	5.0	5.0	5.0
Emissivity	0.06	0.06	0.05	0.05	0.05	0.05	0.06	0.06	0.05	0.05	0.05

Table 2 (unit of layer thickness: nm)

	Examples								Comp. Ex.				
	11	12	13	14	15	16	17	2	3	4	5		
7. Top coat(SiN _x)	-	-	-	-	-	-	-	1	5	-	-		
6. Titania layer	33	33	33	33	33	33	33	33	33	33	33		
5. SiN _x interlayer	-	-	0.5	1	2	3	5	-	-	-	-		
4. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14		
3. SiN _x interlayer	3	5	0.5	1	2	3	5	-	-	-	-		
2. Titania layer	33	33	33	33	33	33	33	33	33	33	33		
1. Bottom coat (SiN _x)	-	-	-	-	-	-	-	-	-	1	5		
Visible light transmittance (%)	83.4	83.3	84.5	84.5	84.6	84.4	84.7	82	81.8	81.8	82		
Visible light reflectance (%)	4.6	4.6	4.6	4.5	4.6	4.7	4.6	4.8	4.9	4.7	4.7		
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	5.0	4.9	5.0	4.9	5.0	5.0	5.0	5.0		
Emissivity	0.05	0.05	0.06	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06		

Table 3 (unit of layer thickness: nm)

	Examples											Comp. Ex.
	1	2	4	5	18	19	8	11	12	20	21	
5. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33
4. SiN ₂	0.5	1	3	5	8	10	-	-	-	-	-	-
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14	14
2. SiN ₂	-	-	-	-	-	-	1	3	5	8	10	-
1. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33
Pencil scratch value	3H	4H	6H	6H	7H	7H	H	H	H	H	H	B
Laminate	A-1	A-2	A-4	A-5	A-18	A-19	A-8	A-11	A-12	A-20	A-21	B-1

Table 4 (No. 1)

(unit of layer thickness: nm)

	Comp. Ex.	Examples									
		22	23	24	25	26	27	28	29	30	31
11. Top coat (SiN _x)	-	-	-	-	-	-	-	-	-	-	-
10. Titania layer	33	33	33	33	33	33	33	33	33	33	33
9. SiN _x interlayer	-	-	-	-	-	-	-	1	5	-	-
8. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14
7. SiN _x interlayer	-	-	-	-	-	1	5	-	-	1	5
6. Titania layer	66	66	66	66	66	66	66	66	66	66	66
5. SiN _x interlayer	-	-	-	1	5	-	-	-	-	-	-
4. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14
3. SiN _x interlayer	-	1	5	-	-	-	-	-	-	1	5
2. Titania layer	33	33	33	33	33	33	33	33	33	33	33
1. Bottom coat (SiN _x)	-	-	-	-	-	-	-	-	-	-	-
Visible light transmittance (%)	68	69.4	69.3	69.6	70.2	70.1	70.3	70.3	70.4	71.4	71.8
Visible light reflectance (%)	6.2	6.2	6.1	6.1	6.2	6.2	6.3	6.2	6.3	6.2	6.3
Sheet resistance value (Ω/\square)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Emissivity	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

Table 4 (No. 2)

[illegible]

Table 4 (No. 3) (unit of layer thickness: nm)

	Examples			Comp. Ex.
	38a	39a	40a	6a
11. Top coat (SiN _x)	-	-	-	-
10. Titania layer	33	33	33	33
9. SiN _x interlayer	1	3	5	-
8. Ag-1 at% Pd-1 at% Cu layer	14	14	14	14
7. SiN _x interlayer	1	3	5	-
6. Titania layer	66	66	66	66
5. SiN _x interlayer	1	3	5	-
4. Ag-1 at% Pd-1 at% Cu layer	14	14	14	14
3. SiN _x interlayer	1	3	5	-
2. Titania layer	33	33	33	33
1. Bottom coat (SiN _x)	-	-	-	-
Visible light transmittance (%)	74.1	74.0	74.0	67.8
Visible light reflectance (%)	6.3	6.2	6.3	6.2
Sheet resistance value (Ω/\square)	2.5	2.5	2.5	2.5
Emissivity	0.03	0.03	0.03	0.03

Table 4 (No. 4) (unit of layer thickness: nm)

	Examples			Comp. Ex.
	38b	39b	40b	6b
11. Top coat (SiN _x)	-	-	-	-
10. Titania layer	33	33	33	33
9. SiN _x interlayer	1	3	5	-
8. Ag-1 at% Au layer	14	14	14	14
7. SiN _x interlayer	1	3	5	-
6. Titania layer	66	66	66	66
5. SiN _x interlayer	1	3	5	-
4. Ag-1 at% Au layer	14	14	14	14
3. SiN _x interlayer	1	3	5	-
2. Titania layer	33	33	33	33
1. Bottom coat (SiN _x)	-	-	-	-
Visible light transmittance (%)	76.3	76.4	76.3	70.1
Visible light reflectance (%)	6.2	6.2	6.3	6.2
Sheet resistance value (Ω/\square)	2.2	2.2	2.2	2.2

Table 5

	Examples		
	38	41	42
Visible light transmittance (%)	74.3	74.2	72.3
Visible light reflectance (%)	6.3	1.1	1.1
Transmittance of light having a wavelength of 900 nm (%)	14.5	9.5	4.6
Sheet resistance value (Ω/\square)	2.5	2.5	2.5

Table 6

	Examples						Comp. Ex. 6
	24	25	28	29	32	33	
Pencil scratch value	2H	2H	4H	5H	5H	6H	B

Table 7 (unit of layer thickness: nm)

	Examples			Comp. Ex.
	43	44	45	7
13. Titania layer	30	30	30	30
12. SiN _x interlayer	1	-	1	-
11. Ag-1 at% Pd layer	16	16	16	16
10. SiN _x interlayer	-	1	1	-
9. Titania layer	55.5	55.5	55.5	55.5
8. SiN _x interlayer	1	-	1	-
7. Ag-1 at% Pd layer	16	16	16	16
6. SiN _x interlayer	-	1	1	-
5. Titania layer	55.5	55.5	55.5	55.5
4. SiN _x interlayer	1	-	1	-
3. Ag-1 at% Pd layer	16	16	16	16
2. SiN _x interlayer	-	1	1	-
1. Titania layer	30	30	30	30
Visible light transmittance (%)	64.4	64.2	68.5	59.6
Visible light reflectance (%)	6.6	6.6	6.7	6.5
Sheet resistance value (Ω/\square)	1.5	1.5	1.5	1.5

Table 8

	Examples		
	45	46	47
Visible light transmittance (%)	68.5	68.6	67.0
Visible light reflectance (%)	6.7	1.7	1.5
Transmittance of light having a wavelength of 900 nm (%)	2.4	2.3	0.01
Sheet resistance value (Ω/\square)	1.5	1.5	1.5

Table 9 (unit of layer thickness: nm)

	Examples										Comp. Ex.		
	48	49	50	51	52	53	54	9	10	11			
17. Titania layer	30	30	30	30	30	30	30	30	30	30			
16. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
15. Ag-1 at% Pd layer	20	18	17	20	20	20	20	20	18	17			
14. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
13. Titania layer	57	57	57	57	57	57	57	57	57	57			
12. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
11. Ag-1 at% Pd layer	26	23	19	26	26	26	26	26	23	19			
10. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
9. Titania layer	54	54	54	54	54	54	54	54	54	54			
8. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
7. Ag-1 at% Pd layer	26	24	19	26	26	26	26	26	24	19			
6. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
5. Titania layer	57	54	54	57	57	57	57	57	54	54			
4. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
3. Ag-1 at% Pd layer	20	17	17	20	20	20	20	20	17	17			
2. SiN _x interlayer	1	1	1	2	3	4	5	-	-	-			
1. Titania layer	30	30	30	30	30	30	30	30	30	30			
Visible light transmittance (%)	43.8	49.5	55.6	43.8	43.6	44.0	44	28.4	34	39.4			
Visible light reflectance (%)	7.8	7.2	7	7.8	7.9	8.0	8.1	6.8	6.7	6.5			
Sheet resistance value (Ω/\square)	0.5	0.7	0.9	0.5	0.5	0.5	0.5	0.5	0.7	0.9			

Table 10

	Examples			Comp. Ex.		
	55	56	57	12	13	14
Visible light transmittance (%)	44	49.5	55.6	28.4	34	39.4
Visible light reflectance (%)	2.5	2.2	2	1.8	1.7	1.5
Transmittance of light having a wavelength of 900 nm (%)	0.0	0.0	0.28	0.0	0.0	0.3
Sheet resistance value (Ω/\square)	0.5	0.7	0.9	0.5	0.7	0.9

Table 11

(unit of layer thickness: nm)

	Examples				
	58	59	60	61	62
5. Titania layer	33	33	33	33	33
4. SiN _x interlayer	2.0	3.0	2.0	2.5	3.0
3. Ag-1 at% Pd layer	14	14	14	14	14
2. SiN _x interlayer	-	-	2.0	2.5	3.0
1. First (TiO ₂) layer	33	33	33	33	33
Visible light transmittance (%)	83.3	83.3	84.8	84.9	84.7
Visible light reflectance (%)	4.8	4.8	4.8	4.7	4.8
Sheet resistance value (Ω/\square)	5.0	4.9	5.1	5.1	5
Emissivity	0.06	0.06	0.06	0.06	0.06

Table 12 (unit of layer thickness: nm)

	Comp. Ex.	
	15	16
5. Titania layer	33	31.5
4. Ti Layer	-	1.5
3. Ag-1 at% Pd layer	14	14
2. SiN _x interlayer	-	-
1. First (TiO ₂) layer	33	33
Visible light transmittance (%)	79.8	81.6
Visible light reflectance (%)	5.6	5.1
Sheet resistance value (Ω/\square)	520	4.9
Emissivity	8.2	0.06

Table 13 (No. 1) (unit of layer thickness: nm)

	Examples										
	63	64	65	66	67	68	69	70	71	72	
5. Titania layer	33	33	33	33	33	33	33	33	33	33	
4. GZO interlayer	0.5	1	1.5	2	2.5	3	-	-	-	-	
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	
2. GZO interlayer	-	-	-	-	-	-	0.5	1	1.5	2	
1. Titania layer	33	31	31	30	33	33	33	33	33	33	
Visible light transmittance (%)	83.1	83.0	83.2	83.3	83.2	83.2	83.2	83.1	83.1	83.2	
Visible light reflectance (%)	4.8	4.8	4.9	4.9	4.9	4.9	4.8	4.8	4.9	4.9	
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	5.0	5.0	4.9	5.0	5.0	5.0	5.0	
Emissivity	0.06	0.04	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.06	

Table 13 (No. 2) (unit of layer thickness: nm)

	Examples									Comp. Ex.
	73	74	75	76	77	78	79	80		
5. Titania layer	33	33	33	33	33	33	33	33	1	
4. GZO interlayer	0.5	1	1.5	2	2.5	3	4	5	-	
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	
2. GZO interlayer	0.5	1	1.5	2	2.5	3	4	5	-	
1. Titania layer	33	31	31	30	33	33	33	33	33	
Visible light transmittance (%)	84.7	84.7	84.8	84.7	84.8	84.9	85.0	84.8	81.4	
Visible light reflectance (%)	4.9	4.8	4.9	5.0	4.9	4.9	5.0	5.0	5.0	
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	5.0	4.9	4.9	4.9	4.8	5.0	
Emissivity	0.06	0.05	0.05	0.05	0.06	0.06	0.05	0.05	0.06	

Table 14 (No. 1) (unit of layer thickness: nm)

	Examples												
	64	66	68	81	82	83	84	85	86	87	88	89	
5. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33	
4. GZO interlayer	1	2	3	4	5	6	8	10	12.5	15	17.5	20	
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14	14	
2. GZO interlayer	-	-	-	-	-	-	-	-	-	-	-	-	
1. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33	
Pencil scratch value	H	H	H	H	4H	4H	4H	5H	5H	6H	6H	6H	
Laminate	A-64	A-66	A-68	A-81	A-82	A-83	A-84	A-85	A-86	A-87	A-88	A-89	

Table 14 (No. 2)

(unit of layer thickness: nm)

	Examples													Comp. Ex.
	70	72	90	91	92	93	94	95	96	97	98	99	100	
5. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33	33	1
4. GZO interlayer	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14	14	14	14
2. GZO interlayer	1	2	3	4	5	6	7	8	9	10	11	12	13	-
1. Titania layer	33	33	33	33	33	33	33	33	33	33	33	33	33	33
Pencil scratch value	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	B
Laminate	A-70	A-72	A-90	A-91	A-92	A-93	A-94	A-95	A-96	A-97	A-98	A-99	A-100	B-1

Table 15 (No. 1) (unit of layer thickness: nm)

	Examples										
	101	102	103	104	105	106	107	108	109	110	111
9. Titania layer	33	33	33	33	33	33	33	33	33	33	33
8. GZO interlayer	-	-	-	-	-	-	1	3	-	-	1
7. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14
6. GZO interlayer	-	-	-	-	1	3	-	-	1	3	-
5. Titania layer	66	66	66	66	66	66	66	66	66	66	66
4. GZO interlayer	-	-	1	3	-	-	-	-	-	-	1
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14	14
2. GZO interlayer	1	3	-	-	-	-	-	-	1	3	-
1. Titania layer	33	33	33	33	33	33	33	33	33	33	33
Visible light transmittance (%)	69.3	69.4	69.7	70.0	69.4	69.6	69.5	69.5	71.0	71.3	72
Visible light reflectance (%)	6.2	6.2	6.2	6.2	6.2	6.3	6.2	6.3	6.2	6.2	6.2
Sheet resistance value (Ω/\square)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Emissivity	0.04	0.05	0.03	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.03

Table 15 (No. 2)

(unit of layer thickness: nm)

	Examples											Comp. Ex.
	112	113	114	115	116	117	118	119	120	121		
9. Titania layer	33	33	33	33	33	33	33	33	33	33		6
8. GZO interlayer	3	-	-	1	3	0.5	1	2	3	5		-
7. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14		14
6. GZO interlayer	-	-	-	1	3	0.5	1	2	3	5		-
5. Titania layer	66	66	66	66	66	66	66	66	66	66		66
4. GZO interlayer	3	1	3	-	-	0.5	1	2	3	5		-
3. Ag-1 at% Pd layer	14	14	14	14	14	14	14	14	14	14		14
2. GZO interlayer	-	1	3	-	-	0.5	1	2	3	5		-
1. Titania layer	33	33	33	33	33	33	33	33	33	33		33
Visible light transmittance (%)	72	71.2	71.4	71.2	71.9	74.8	74.9	75.3	75.1	75.3		68.0
Visible light reflectance (%)	6.3	6.1	6.2	6.2	6.3	6.2	6.2	6.3	6.4	6.5		6.2
Sheet resistance value (Ω/\square)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.4	2.4		2.5
Emissivity	0.03	0.04	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.03		0.04

Table 16

(unit of layer thickness: nm)

	Examples					Comp. Ex.
	122	123	124	125	126	1
5. Titania layer	33	33	33	33	33	33
4. NbO _x interlayer	-	-	-	-	-	-
3. Ag-1 at% Pd layer	14	14	14	14	14	14
2. NbO _x interlayer	0.5	1	2	3	4	-
1. Titania layer	33	33	33	33	33	33
Visible light transmittance (%)	82.8	82.7	83.2	82.9	82.9	81.4
Visible light reflectance (%)	4.9	4.9	4.9	5.0	5.0	5.0
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	5.0	5.0	5.0
Emissivity	0.06	0.06	0.06	0.05	0.05	0.06

Table 17

(unit of layer thickness: nm)

	Examples					Comp. Ex.
	127	128	129	130	131	1
5. Titania layer	33	33	33	33	33	33
4. ITO interlayer	-	-	-	-	-	-
3. Ag-1 at% Pd layer	14	14	14	14	14	14
2. ITO interlayer	1	1.5	2	3	4	-
1. First (TiO ₂) layer	33	33	33	33	33	33
Visible light transmittance (%)	82.8	82.9	83.1	83	83.1	81.4
Visible light reflectance (%)	4.9	4.9	4.9	5.0	5.0	5.0
Sheet resistance value (Ω/\square)	5.0	5.0	5.0	5.0	4.9	5.0
Emissivity	0.06	0.06	0.06	0.05	0.05	0.06

CLAIMS

1. A laminate which comprises a substrate, and a titanium oxide layer, a metal layer and a titanium oxide layer laminated alternately in this order on the substrate in $(2n + 1)$ layers (wherein n is a positive integer), wherein an interlayer having a refractive index of less than 2.4 at a wavelength of 550 nm is interposed at at least one interlaminar boundary between the titanium oxide layer and the metal layer.
2. The laminate according to Claim 1, wherein each of the titanium oxide layers has a refractive index of at least 2.4 at a wavelength of 550 nm.
3. The laminate according to Claim 1 or 2, wherein the interlayer is a layer consisting of at least one member selected from the group consisting of an oxide, a nitride, an oxynitride, a carbide and a boride.
4. The laminate according to any one of Claims 1 to 3, wherein the thickness of the interlayer is from 0.1 to 30 nm.
5. The laminate according to any one of Claims 1 to 4, wherein the metal layer is a layer containing at least one metal selected from the group consisting of silver, copper and gold.
6. The laminate according to any one of Claims 1 to 5, wherein the sheet resistance value is from 0.5 to 3.5 Ω/\square , the visible light transmittance is at least 40%, and the visible light reflectance is at most 10%.

7. The laminate according to any one of Claims 1 to 6, wherein a resin film having a low-reflecting property is further laminated thereon.

8. The laminate according to any one of Claims 1 to 7,
5 wherein a resin film having an near-infrared shielding property is further laminated thereon.

9. The laminate according to any one of Claims 5 to 8, wherein the visible light reflectance is at most 3%.

10. A method for producing a laminate comprising a
10 substrate, and a titanium oxide layer, a metal layer and a titanium oxide layer laminated alternately in this order on the substrate in $(2n + 1)$ layers (wherein n is a positive integer), which comprises a step of interposing an interlayer having a refractive index of less than 2.4
15 at a wavelength of 550 nm at at least one interlaminar boundary between the titanium oxide layer and the metal layer.

ABSTRACT

A laminate having improved visible light transmittance and abrasion resistance, which comprises a substrate, and a titanium oxide layer, a metal layer and a titanium oxide layer laminated alternately in this order on the substrate in $(2n + 1)$ layers (wherein n is a positive integer), wherein an interlayer having a refractive index of less than 2.4 at a wavelength of 550 nm is interposed at at least one interlaminar boundary between the titanium oxide layer and the metal layer.

Fig. 1

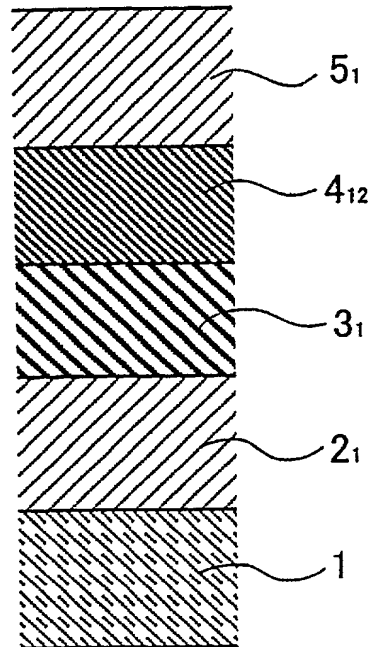


Fig. 2

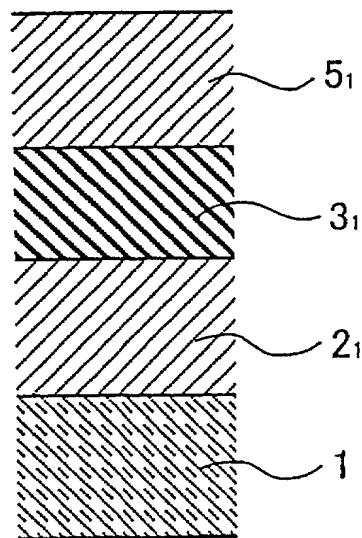


Fig. 3

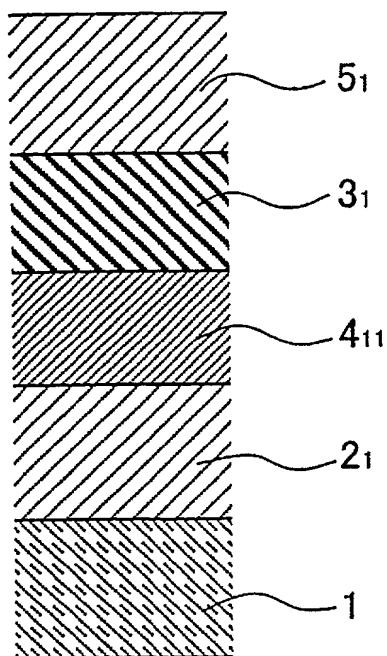
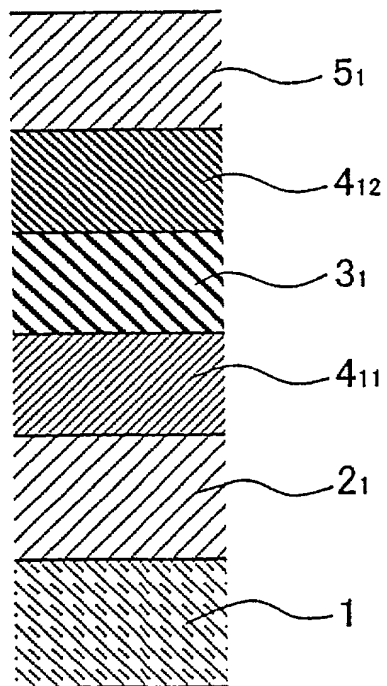
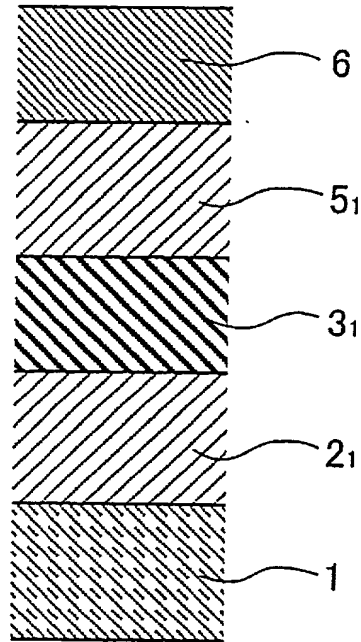


Fig. 4



F i g. 5



F i g. 6

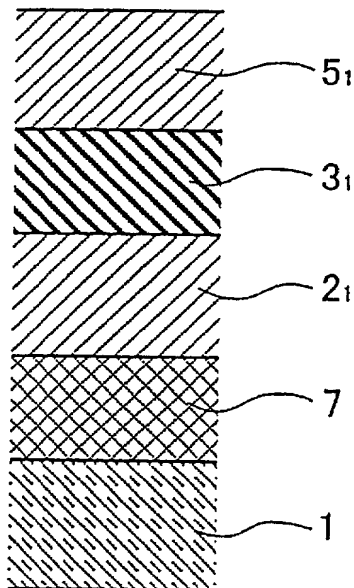


Fig. 7

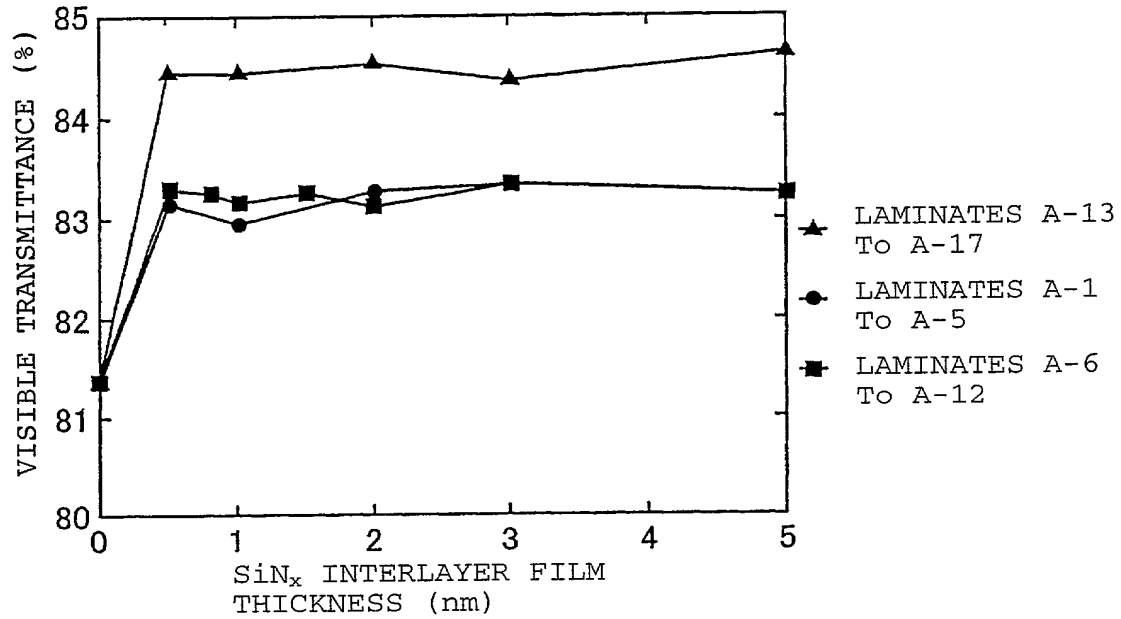


Fig. 8

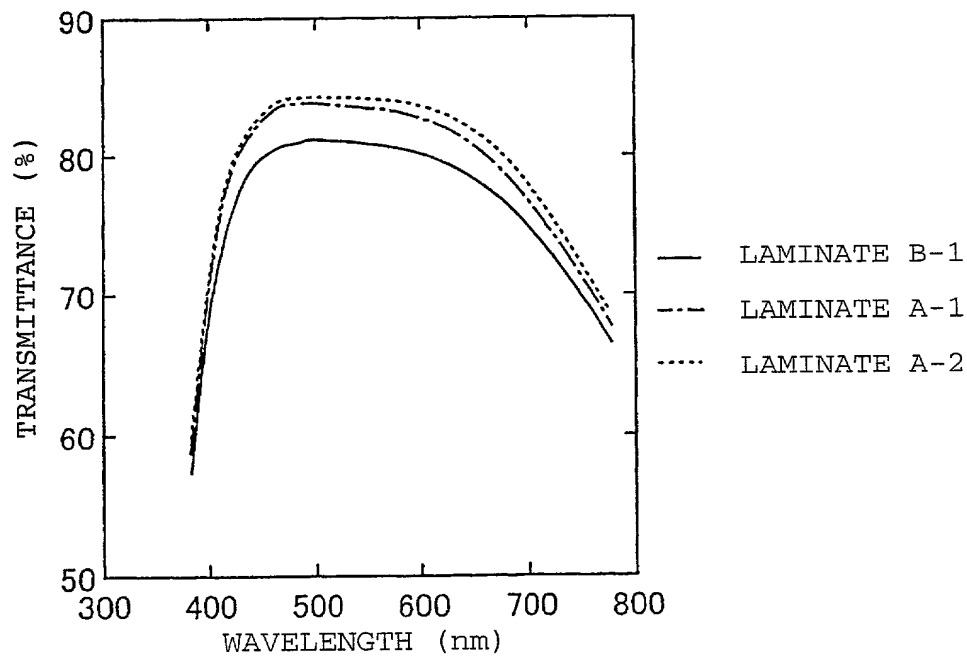


Fig. 9

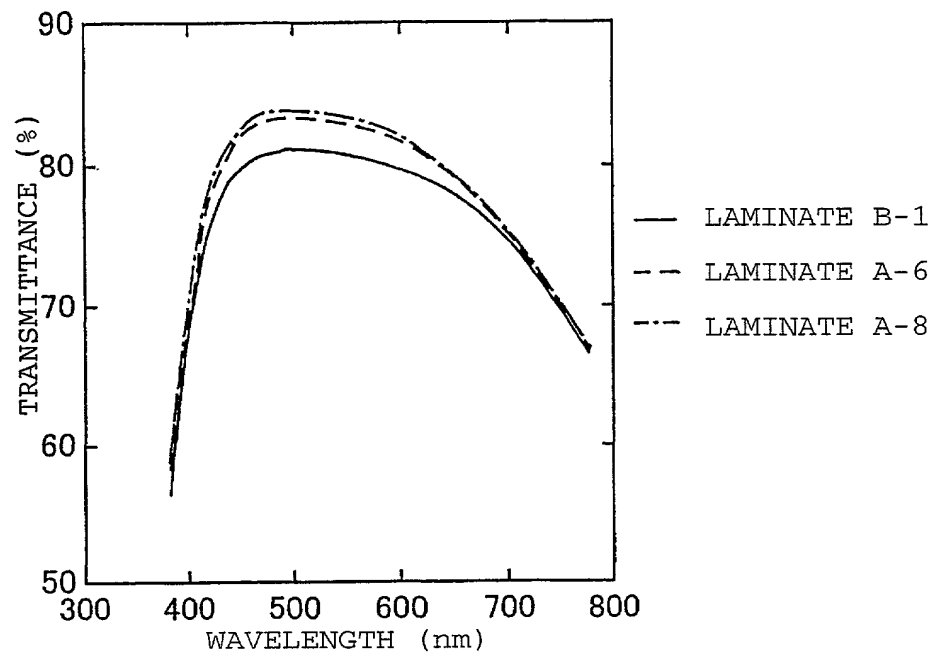


Fig. 10

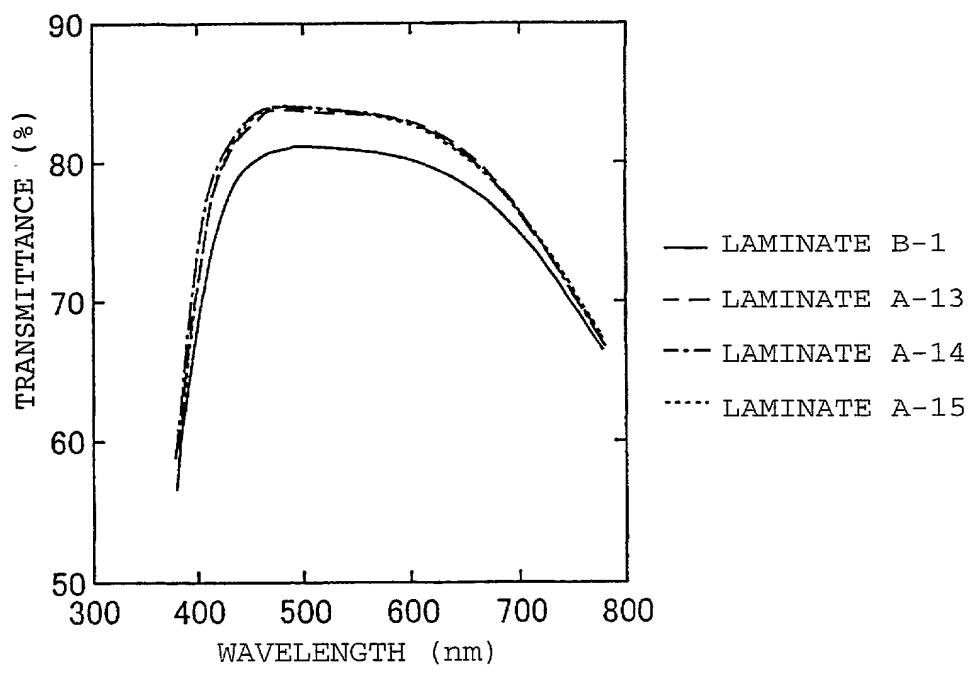


Fig. 11

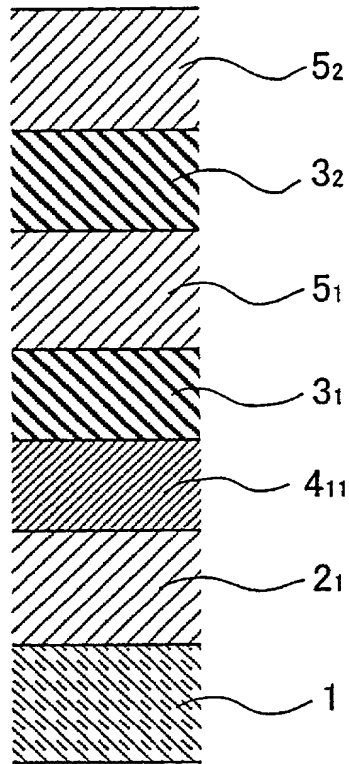


Fig. 12

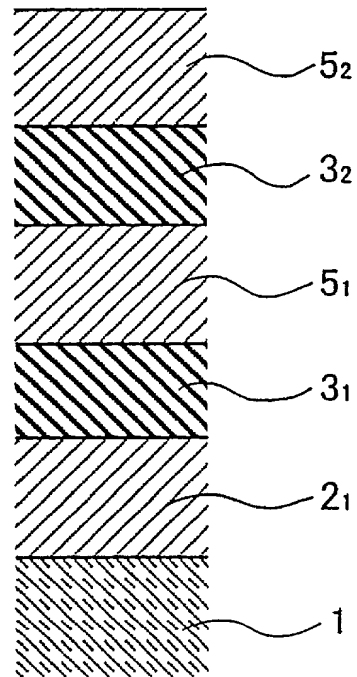




Fig. 13

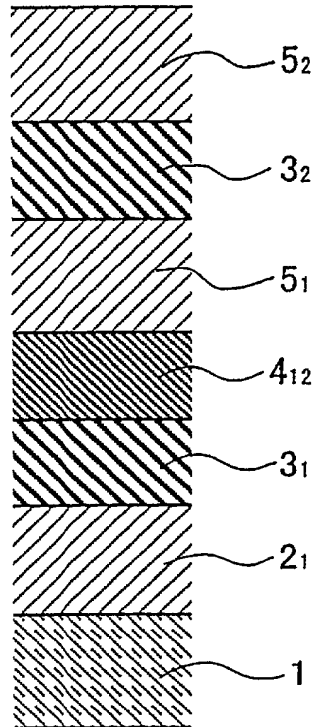


Fig. 14

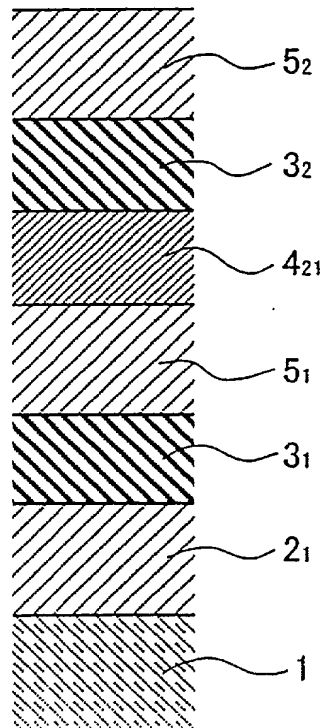


Fig. 15

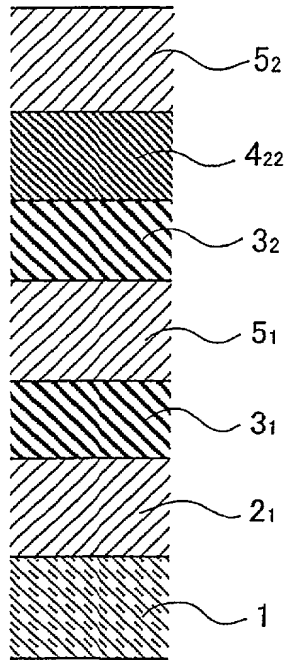


Fig. 16

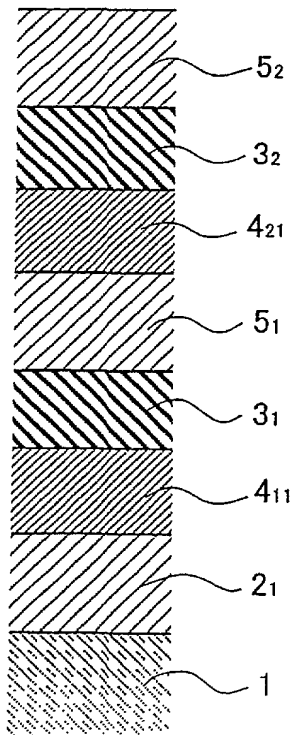




Fig. 17

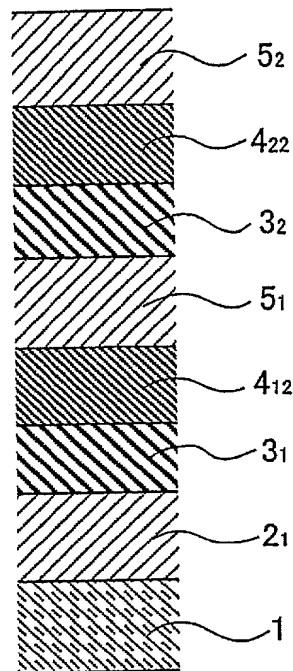


Fig. 18

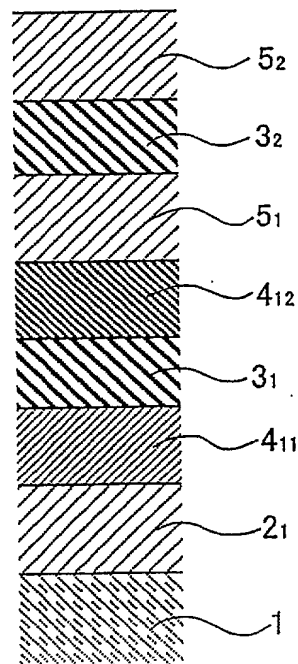


Fig. 19

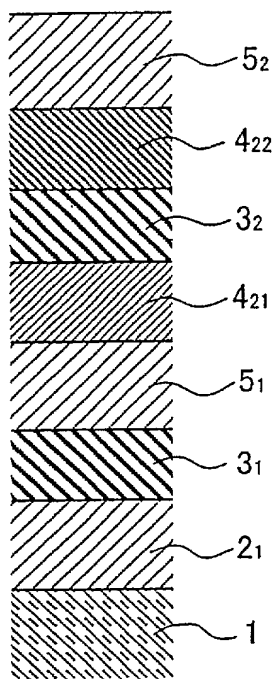


Fig. 20

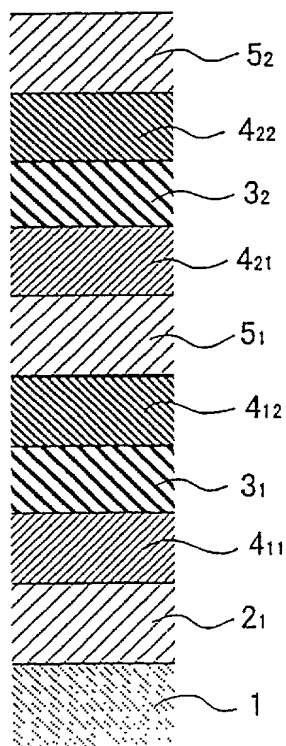
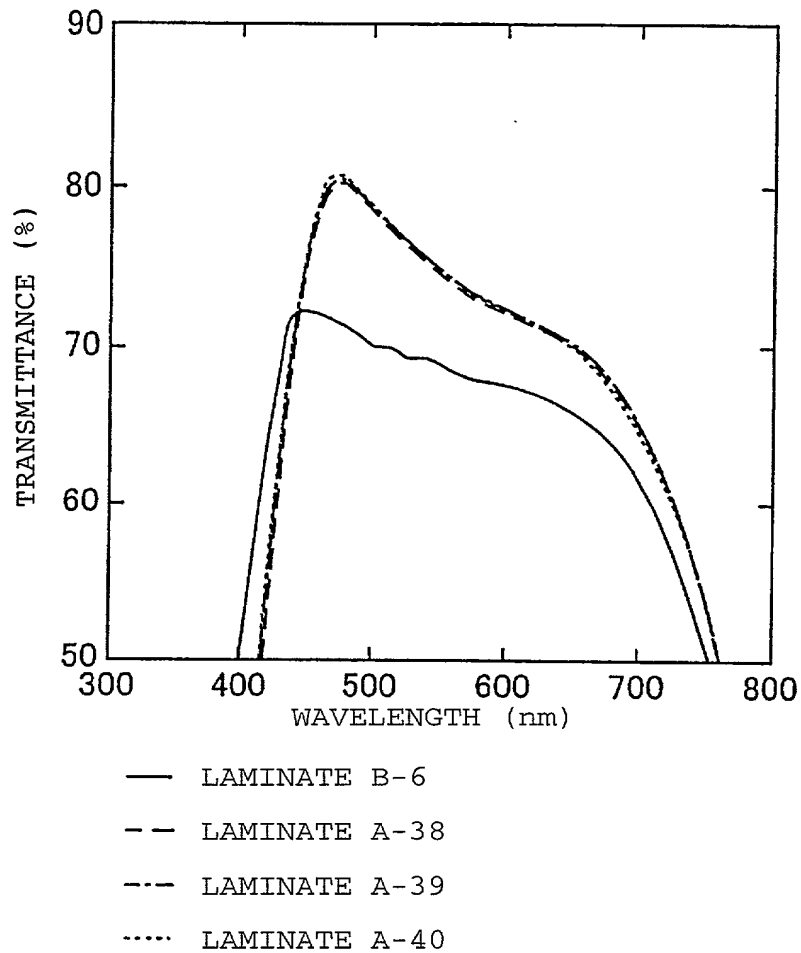




Fig. 21





F i g. 22

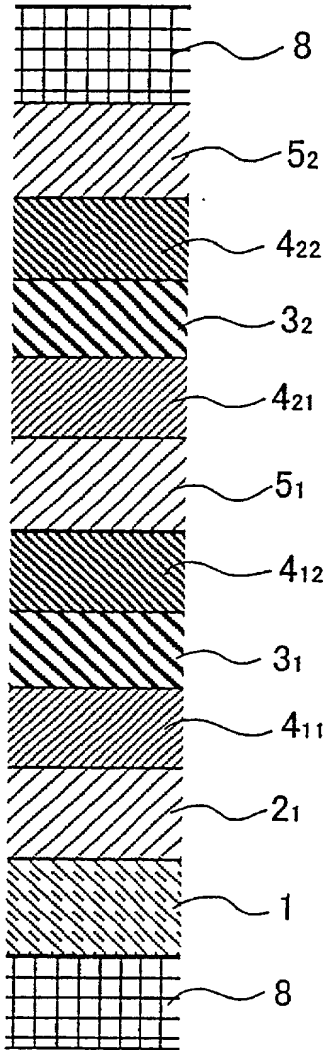


Fig. 23

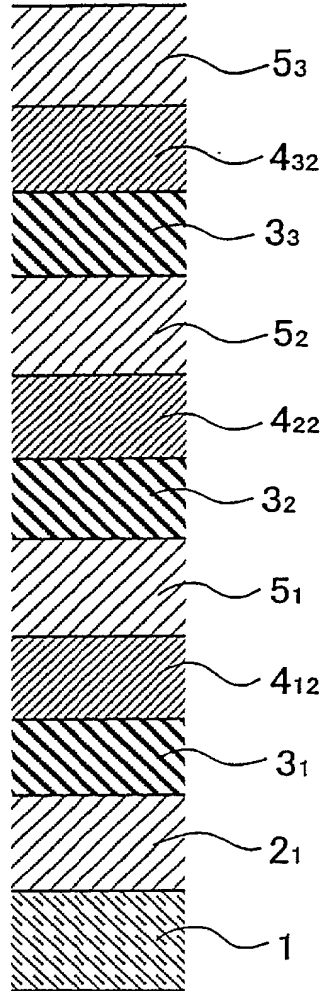




Fig. 24

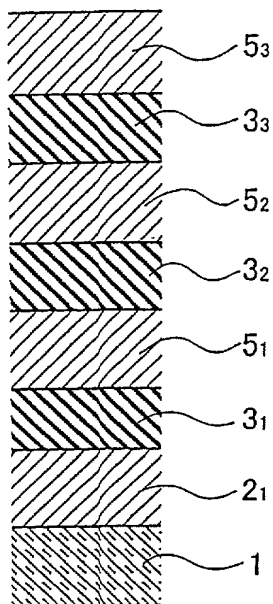


Fig. 25

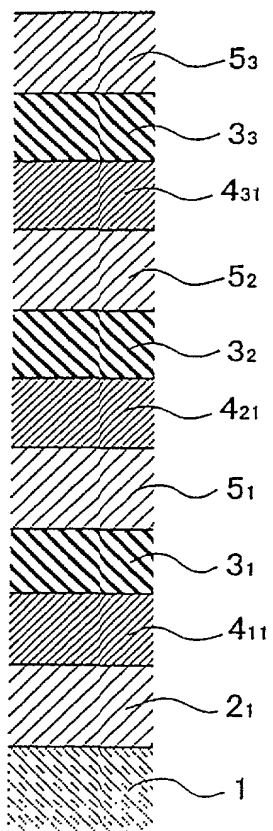




Fig. 26

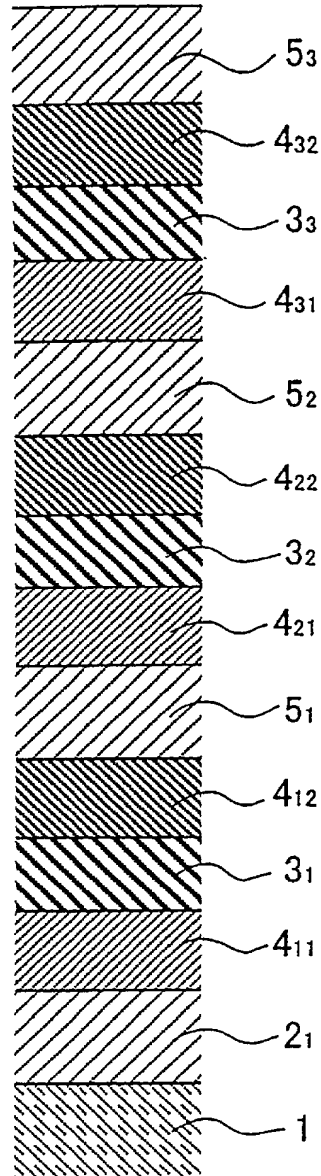




Fig. 27

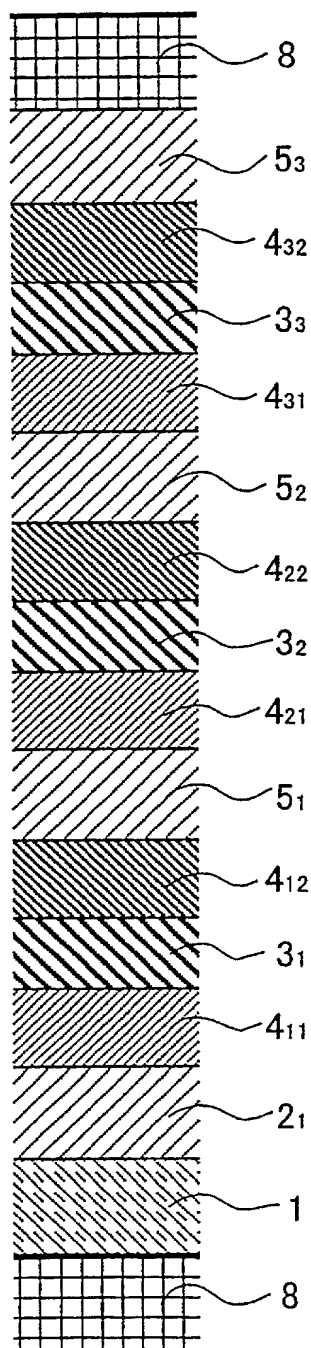




Fig. 28

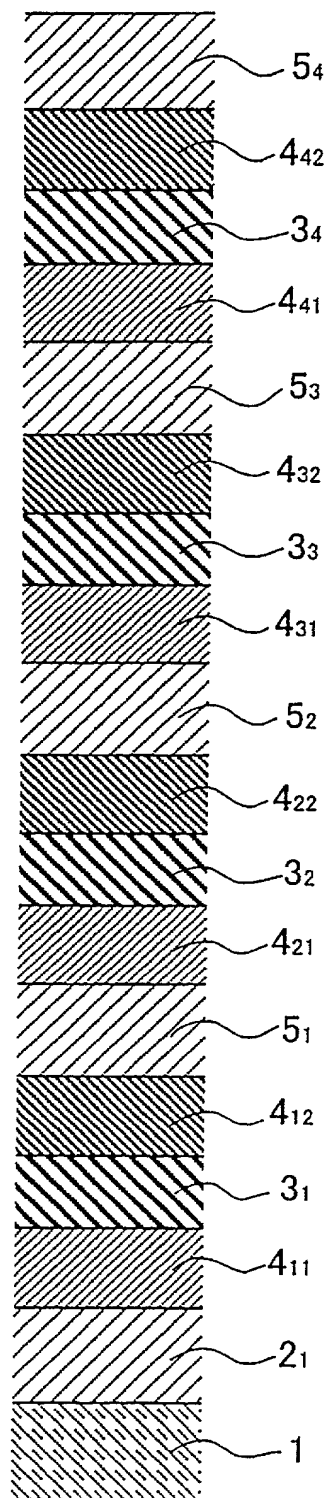


Fig. 29

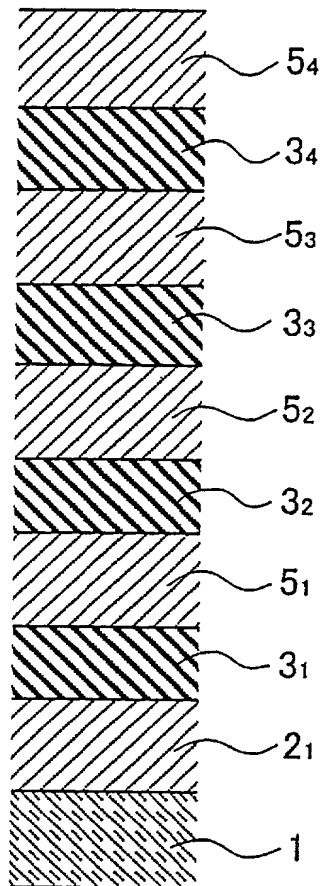


Fig. 30

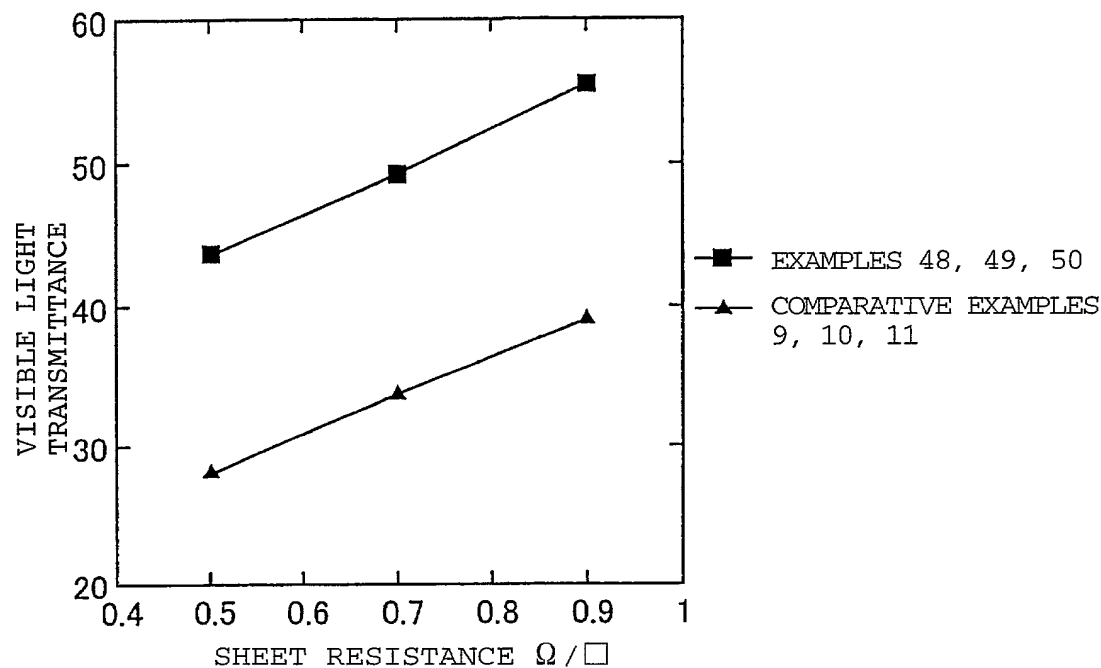


Fig. 31

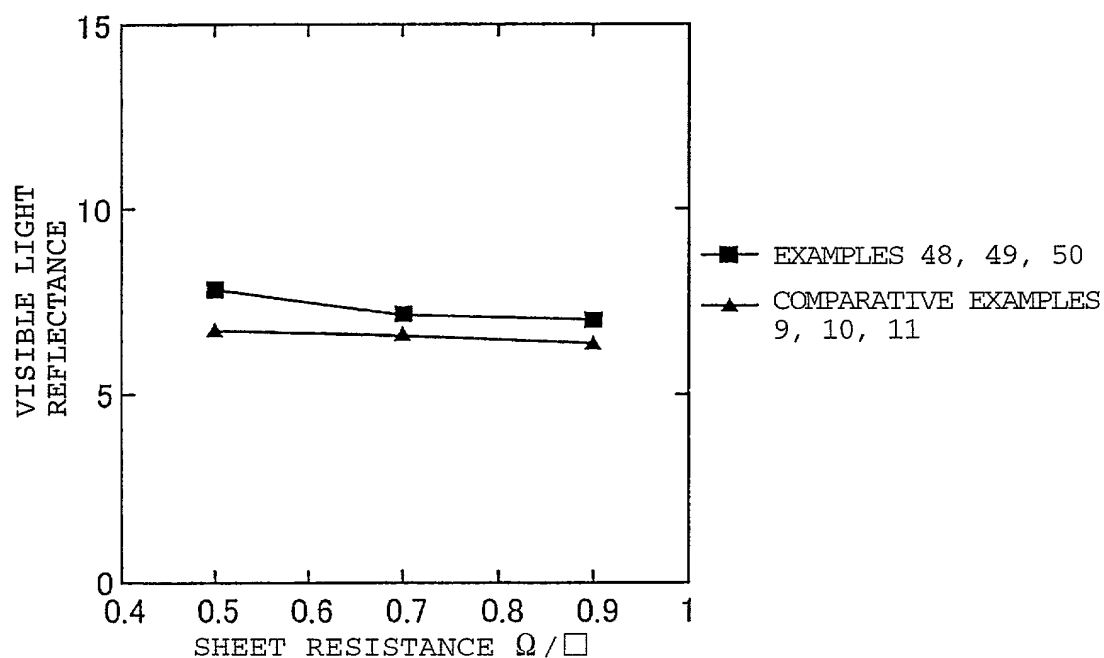




Fig. 32

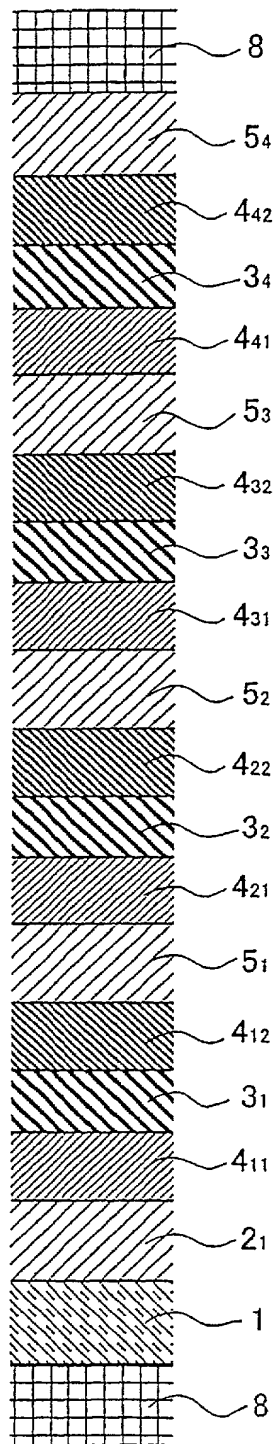




Fig. 33

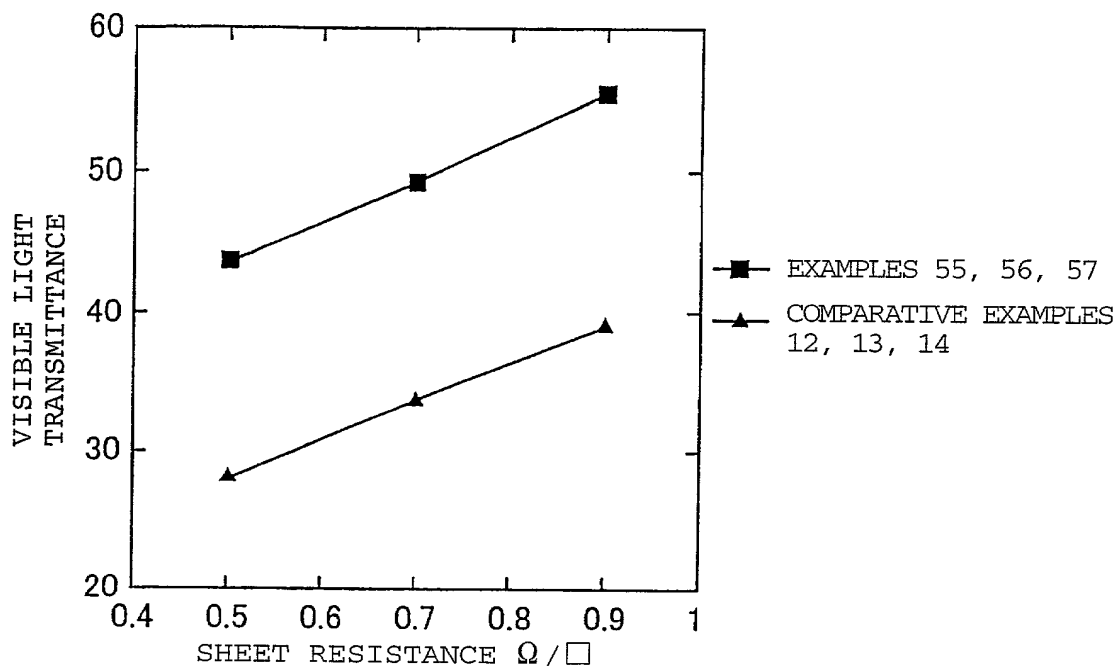
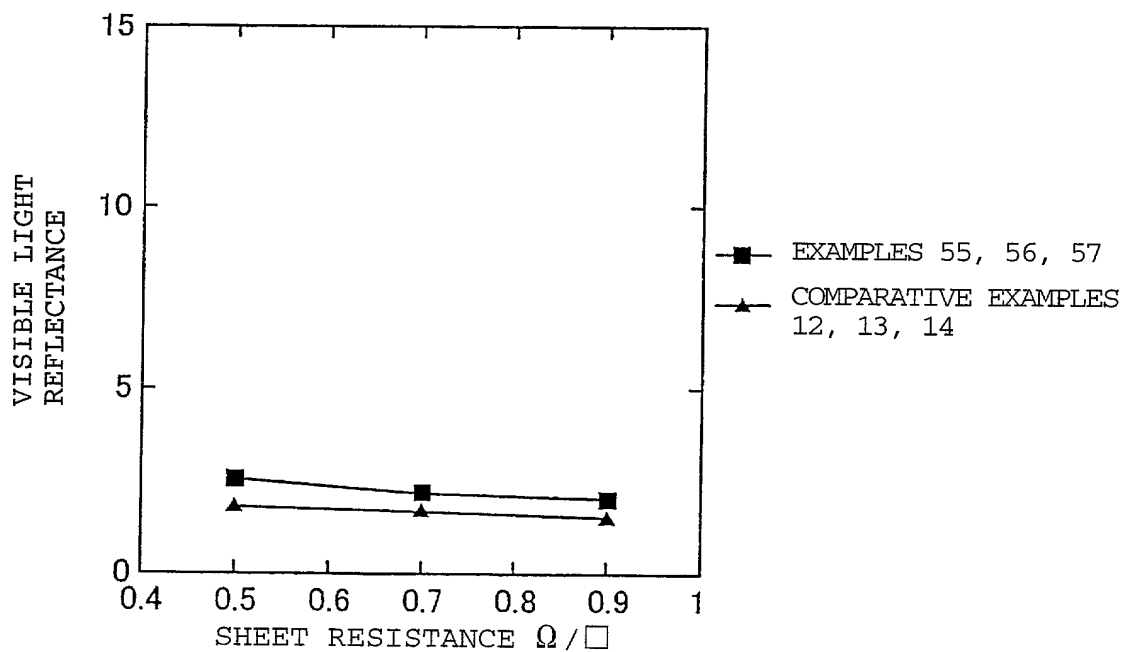


Fig. 34



Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

上記発明の明細書は、

☐ 本書に添付されています。

☐ ____月____日に提出され、米国出願番号または特許協定条約国際出願番号を____とし、
(該当する場合) _____に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

LAMINATE AND ITS PRODUCTION METHOD

the specification of which

☐ is attached hereto.

☒ was filed on December 27, 1999
as United States Application Number or
PCT International Application Number
PCT/JP99/07344 and was amended on
_____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)
外国での先行出願

10-374186

Japan

(Number)
(番号)

(Country)
(国名)

(Number)
(番号)

(Country)
(国名)

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)
(出願番号)

(Filing Date)
(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

PCT/JP99/07344

December 27, 1999

(Application No.)
(出願番号)

(Filing Date)
(出願日)

(Application No.)
(出願番号)

(Filing Date)
(出願日)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じることに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed
優先権主張

28/December/1998

(Day/Month/Year Filed)
(出願年月日)

☒ Yes
はい

☐ No
いいえ

(Day/Month/Year Filed)
(出願年月日)

☐ Yes
はい

☐ No
いいえ

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)
(出願番号)

(Filing Date)
(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

Pending

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
(弁理士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



022850

書類送付先

Send Correspondence to:



022850

直接電話連絡先：(名前及び電話番号)

Direct Telephone Calls to: (name and telephone number)
(703) 413-3000

単独発明者または第一の共同発明者の氏名	1-00	Full name of sole or first joint inventor	Yuko Tachibana
発明者の署名	日付	Inventor's signature	Yuko Tachibana May 30, 2001
住所		Residence	Kanagawa, Japan JPX
国籍		Citizenship	Japanese
郵便の宛先		Post Office Address	c/o Asahi Glass Company, Limited, 1150, Hazawa-cho, Kanagawa-ku, Yokohama-shi, KANAGAWA 221-8755 JAPAN
第二の共同発明者の氏名	2-00	Full name of second joint inventor, if any	Hisashi Ohsaki
第二の共同発明者の署名	日付	Second joint inventor's signature	Hisashi Ohsaki May 30, 2001
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国籍		Citizenship	Japanese
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(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)